How Herbicides Work

Biology to Application
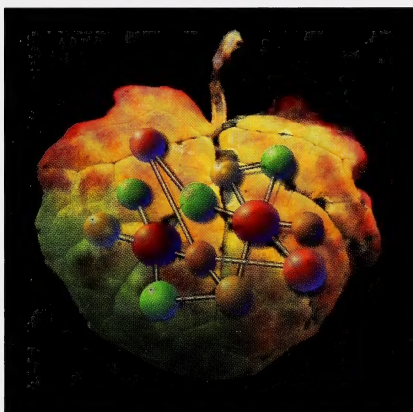
Alberta
AGRICULTURE, FOOD AND
RURAL DEVELOPMENT

How Herbicides Work

Biology to Application

Linda Hall
Plant Industry Division
Alberta Agriculture, Food and Rural Development

Hugh Beckie
Saskatoon Research Centre
Agriculture and Agri-Food Canada

Thomas M. Wolf
Saskatoon Research Centre
Agriculture and Agri-Food Canada

Contents

Herbicide Resistance 63

Acknowledgments

Foreword

This book provides a base for understanding herbicide action and discusses key aspects of their application. Specific information about a few of the important herbicide groups gives a solid background on the biology of these important weed control tools. Discussion about the dose transfer process, adjuvants and herbicide spray drift concerns gives the book a strong focus on the practical application of herbicides.

Weed science and spray technology are dynamic. The understanding of herbicide mechanisms of action and their application changes with each new herbicide and each new research paper. The book sacrifices some detail to provide you with a broader overview. For example, herbicide groups are discussed, but individual herbicides within those groups may vary. The text covers low-drift spray nozzles; however, more detailed technical information on the particular nozzle choices can be found in other reference materials. For specifics, consult Alberta Agriculture's *Crop Protection*, Agdex 606-1, the product label or the *Herbicide Handbook*.

One book cannot be a comprehensive source of information on these broad topics. For further information, please consult the references listed in Appendix I.

How Herbicides Work

To be effective, foliar-applied herbicides must:

- **be retained on the leaf**
- **penetrate the waxy cuticular layer on the surface of the leaf**
- **move through the water-filled space around the cell**
- **enter a cell, passing through a lipid-like membrane**
- **reach the target site, usually an enzyme, and**
- **bind to and inhibit the target enzyme**

To be selective, a herbicide must:

- **affect the target site of the weed, but not the crop, or**
- **be metabolized or broken down by the crop plant, and**
- **not be metabolized by the weed, or**
- **reach the target plant, but not the weed**

Herbicides must work reliably when:

- **the crop plants and weeds are growing rapidly, and**
- **the crop plants and weeds are under stress**

One wonders from the above description, not how herbicides work, but why they work at all! This chapter outlines general principles of how herbicides act.

Target sites

Herbicides have a specific target site, a place in the plant that herbicides bind to and inhibit function. Most target sites are enzymes. By binding to the target site, herbicides stop or slow down enzyme function (Figure 1). There are some exceptions. Several common herbicides, such as cyanazine (Group 5) and paraquat (Group 22), which interact with photosynthesis, either block electron transport in Photosystem II or accept electrons from Photosystem I. These are non-enzymatic target sites. The dinitroanalines (Group 3) and the auxinic herbicides (Group 4) are thought to bind to a non-enzyme site.

In most cases, herbicides inhibit only one enzyme or target site. There are thousands of different enzymes in every cell, and usually only one is affected by a herbicide.

In North America, we divide herbicides into groups based on target site. Herbicides that affect the same target site frequently have the same symptoms, application method, constraints and even toxicological profile. Herbicide groups are also an important consideration in managing herbicide resistance.

Herbicides in the same group can vary in the weeds they control and the crops in which they can be used.

What is an enzyme

An enzyme is a protein made up of a chain of amino-acid building blocks folded into a complex three-dimensional shape. Enzymes are catalysts. They facilitate chemical reactions. They reduce the amount of energy required and thus allow thousands of reactions to occur at low temperatures.

It is thought enzymes have active sites, places where substrates (raw material) bind and where they are modified to form the products. Herbicides can also bind to the active sites of enzymes. These herbicides stop the substrate from binding or perhaps the product from leaving. Herbicides may also bind away from the active sites, possibly changing the shape of the enzyme and stopping it from functioning. In this way, herbicides kill plants.

	Target site	Active ingredient	Product names
Group 1	ACCase	clethodim	Select
		clodinafop-propargyl	Harmony, Total*, Horizon, Platinum*
		diclofop-methyl	Hoe-Grass 284, Hoe-Grass II*
		fenoxaprop-p-ethyl	Champion Extra*, Champion Plus*, Fusion*, Laser DF*, Puma, Puma Super, Triumph Plus*
		fluazifop-p-butyl	Fusion*, Venture
		quizalofop-p-ethyl	Assure II, Freedom Gold,* Muster Gold*, Muster Gold II*
		sethoxydim	Poast Flaxmax*, Poast Ultra
		tralkoxydim	Achieve, Achieve Extra*, Prevail*
Group 2	ALS	chlorsulfuron	Telar
		ethametsulfuron-methyl	Muster, Muster Gold*, Muster Gold II*
		flucarbazone-sodium	
		imazamethabenz	Assert 300
		imazamox	Odyssey*
		imazapyr	Arsenal
		imazethapyr	Odyssey*, Pursuit
		metsulfuron-methyl	Ally, Escort
		nicosulfuron	Accent
		rimsulfuron	Prism
		sulfosulfuron	Anthem*, Sundance
		thifensulfuron-methyl	Champion Extra*, Champion Plus*, Freedom Gold*, Harmony Total*, Laser DF*, Refine Extra*, Triumph Plus*
		triasulfuron	Amber, Unity*
		tribenuron-methyl	Champion Extra*, Crossfire *, Express Pack, Harmony Total*, Muster Gold*, Refine Extra*
Group 3	Cell division	ethalfluralin	Edge
		trifluralin	Advance, Bonanza, Fortress*, Heritage, Rival, Treflan

*   contained in a mixture
**   not presently registered

2

	Target site	Active ingredient	Product names
Group 4	Auxin mimics	2,4-D	2,4-D, Attain*, Champion Plus*, Dichlorprop-D*, DyVel DS*, Estaprop*, Prestige*, Thumper*, Tordon 101*, Turboprop*, Weedone CB*
		2,4-DB	2,4-DB, Caliber, Cobutox, Embutox
		2,4-DP	Diphenoprop*, Estaprop*, Weedone CB*
		clopyralid	Curtail M*, Lontrel, Poast Flaxmax*, Prestige*, Prevail*, Transline
		dicamba	Banvel, DyCleer, DyVel*, DyVel DS*, Rustler*,Target*
		fluroxypyr	Attain*, Prestige*
		MCPA	Achieve Extra*, Buctril M*, Champion Plus*, Curtail M*, DyVel*, Laser DF*, MCPA, Mirage*, Platinum*, Poast Flaxmax*, Prevail*, Prestige*, Stampede CM*, Target*, Triumph Plus*, Tropotox*
		MCPB	Tropotox*, Tropotox Plus*
		mecoprop	Compitox, DyVel DS*, Mecoprop, Target*
		picloram	Tordon 22K, Tordon 101*
		quinclorac	Accord
Group 5	PS II	cyanazine	Bladex, Blagal
		metribuzin	Crossfire*, Lexone, Sencor
Group 6	PS I	bentazon	Basagran
		bromoxynil	Achieve Extra*, Buctril M*, Hoe-Grass II*, Platinum*, Thumper*, Torch/Pardner, Unity*
		pyridate	Lentagran
Group 7	PS II	diuron	Karmex DF, Krovar*
		linuron	Afolan, Lorox
Group 8	More than one target	difenzoquat	Avenge 200C
		EPTC	Eptam
		triallate	Avadex BW, Fortress*

*   contained in a mixture
** not presently registered

	Target site	Active ingredient	Product names
Group 9	EPSP Inhibitors	glyphosate	Glyfos, Laredo, Renegade, Roundup, Roundup Fast Forward*, Roundup Transorb, Rustler*, Touchdown, Victor
Group 10	Glutamine synthetase	glufosinate	Roundup Fast Forward*, Liberty
Group 11	IGPD	amitrole	Amitrol-T
Group 15	Unknown	metolachlor	Dual, Primextra Light*
		propyzamide	Kerb 50W
Group 16	Unknown	ethofumesate	Nortron
Group 22	PS I	diquat	Gramoxone PDQ*, Reglone/Reglone Pro, Reglone A
		paraquat	Gramoxone, Gramoxone PDQ*
Group 25	Unknown	flamprop-methyl	Mataven L
Group 28	(4-H PPD)	isoxaflutole	Balance**

* contained in a mixture
** not presently registered
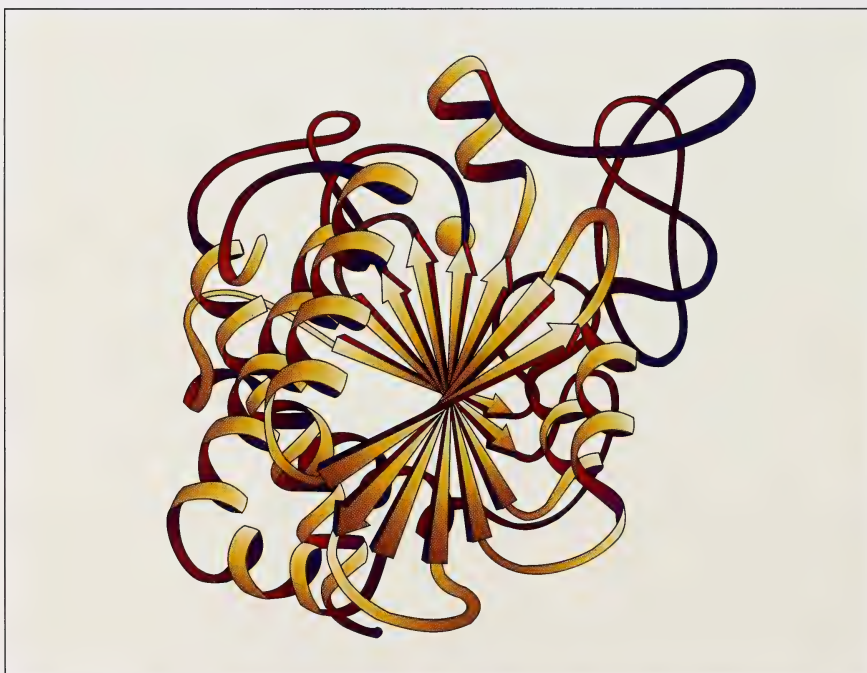
Figure 1. Enzymes are proteins that form complex three-dimensional shapes.

Why herbicides kill plants

While much is known about herbicides and their target sites, it is not always apparent why plants die following a herbicide application.

For example, when plants are treated with an inhibitor of photosynthesis, there is the expectation that the plant will "starve" to death by running out of energy. However, photosynthesis inhibitors work too fast for this to be the case. Photosynthesis inhibitors, by blocking electron movement, produce high energy toxic compounds that destroy membranes and lead to plant death.

It is also possible that by inhibiting enzyme action, a herbicide causes a build-up of a toxic substance. Enzyme activity is normally carefully regulated, so toxic compounds remain at low levels. By inhibiting the target enzyme, the herbicide causes the substance to build up and damage the plant. This is how the herbicide glyphosate (Roundup) works.

In other cases, plant death seems to occur from a de-regulation of the carefully controlled process of cell growth. This is how (Group 4) herbicides, such as 2,4-D, are effective.

For some herbicides, the link between the target site and plant death is not yet understood.

Physical/chemical properties

Herbicides affect a particular target site because they are the right shape, like a key for a specific lock. There are two additional properties that influence effectiveness, particularly how herbicides reach the target site from the soil or the surface of the plant. One is their **solubility properties,** the other is whether they are **weak acids**.

Solubility is a measure of how much herbicides will dissolve in water or organic solvents. A simple analogy may be the difference between oil-based and latex paint. When cleaning paint brushes, water is used to dissolve latex paint, and turpentine or another organic solvent is employed to dissolve oil-based paint. Herbicides are similar. Some dissolve well in water, but not in oil or organic solvents. Glyphosate (Roundup) is a good example of a water-soluble herbicide. Other herbicides dissolve well in organic solvent, but do not dissolve well in water. Diclofop-methyl (Hoegrass) is a good example. When opening a Hoegrass container, the odor of the solvents used to dissolve the diclofop-methyl can be detected.

The measure of solubility is K_{ow}. It is determined by measuring the relative amounts of a herbicide that dissolve in octanol and water. Herbicides with low K_{ow} are water soluable (glyphosate $K_{ow} = 0.0006$). Herbicides with high K_{ow} are soluble in organic solvents (diclofop-methyl $K_{ow} = 37,800$).

The term **weak acid** indicates how readily the chemical, when dissolved in water, will lose a hydrogen ion (H^+), also called a proton. Some chemicals are very miserly and hold onto their protons tightly. Others give up protons readily. Those that give up protons readily are called **weak acids**. The solubility of weak acids depends on the pH

of the solution. The measurement of weak acids is the pKa, the pH at which there are equal amounts of herbicide with and without a protein attached; weak acid herbicides have a pKa less than 7.0.

The manner by which a herbicide's **solubility** and **weak-acid** nature affect how it enters and moves within the plant are discussed below. The K_{ow} and pKa of each herbicide is available in the *Herbicide Handbook*.

Uptake

Herbicides must move from outside the plant, the leaf surface or stem, if foliar-applied, or from the soil solution, if soil-applied, to the target site inside plant cells. The driving force for most herbicide movement is diffusion.

The herbicide pathway is composed of many different media that emulate aqueous solutions or organic-solvents (Figure 2). The cuticle on leaves and stems is waxy; therefore, water-loving (**hydrophilic**) compounds have difficulty dissolving through this layer. Water-hating, oil-soluble (**hydrophobic**) compounds may dissolve into the cuticle and never come out!
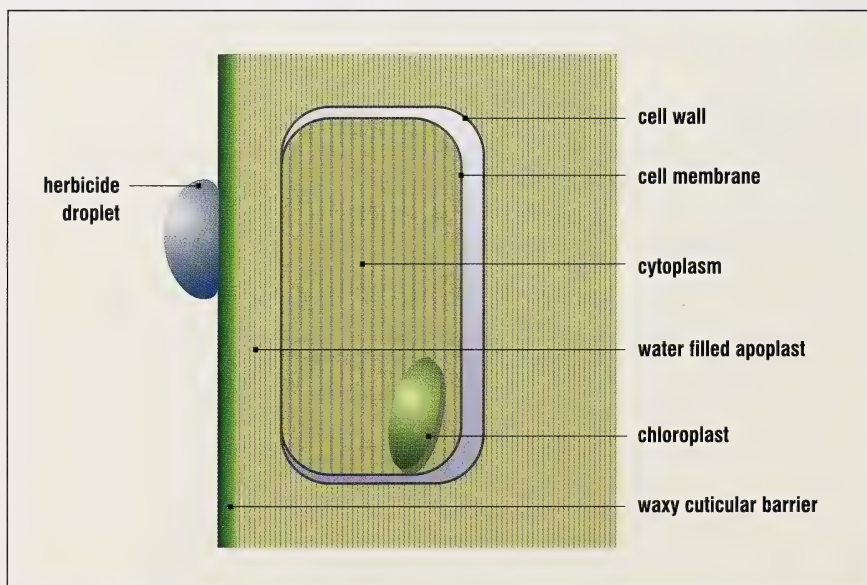
Figure 2. To be effective, a herbicide must move from the outside of the leaf, through many barriers, and reach the target site within the cell.

Next, the herbicide encounters a water-filled area (apoplast) that bathes the cells, and the situation is reversed. Hydrophilic compounds can go into this solution easily, while hydrophobic materials enter and move through slowly. Additionally, water moves through this area, making its way to the edge of the leaves where most is lost to transpiration. Therefore, hydrophilic compounds can get swept along to the edge of the leaves.

Surrounding the cell is a cell membrane. This membrane is primarily made of oil-like substances called phospholipids and some proteins. Hydrophobic herbicides enter the membrane readily, while hydrophilic herbicides enter very slowly. Once dissolved in the oily membrane, hydrophobic herbicides exit slowly, while hydrophilic herbicides exit rapidly.

Inside the cell is a water solution called cytoplasm. Hydrophilic herbicides dissolve readily in the cytoplasm, while hydrophobic herbicides do not.

The alternation of water-like layers with oil-like ones presents problems for both hydrophilic and hydrophobic compounds. Mobile herbicides are therefore **intermediate** between these two extremes. These herbicides have some properties of both, thus having an intermediate solubility that allows them to dissolve in both oil and water to some degree.

The cell membrane, besides keeping the cytoplasm within the cell wall, contains a protein that pumps protons (H^+ or positive charges) from the inside to the outside of the cell. This action makes the outside of the cell more acidic than the inside (Figure 3).
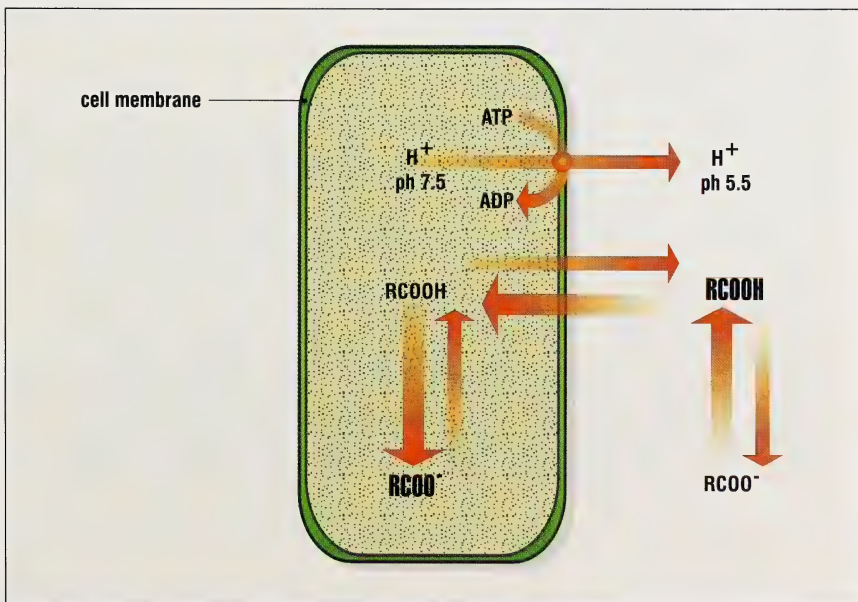
Figure 3. Acid trapping of weak acid herbicides.

The solubility of weak-acid herbicides changes with pH. Outside the cell, weak-acid herbicides tend to accumulate a proton (where they are abundant), making herbicides hydrophobic and able to move through the cell membrane. Inside the cell, weak-acid herbicides lose a proton (they are relatively scarce), making them more hydrophilic or water soluble. Thus, weak-acid herbicides tend to get trapped in cells and accumulate.

Both solubility and weak-acid properties of herbicides affect uptake into cells. They also determine herbicide movement (translocation) in plants.

Translocation

Plants have two transport systems that move nutrients (and sometimes herbicides) throughout the plant (Figure 4).

The xylem system is a one-way stream. It moves water and dissolved minerals from the soil, via roots, to the shoots where water exits the plant. Plants have limited control of xylem movement. The environment, temperature and water availability in soil are major influences on water movement in xylem.

To move in the xylem, a herbicide must be water soluble (as described above). To reach the shoots, soil-applied herbicides usually move in the xylem. The xylem stream can also move foliar-applied herbicides to the edge of leaves.
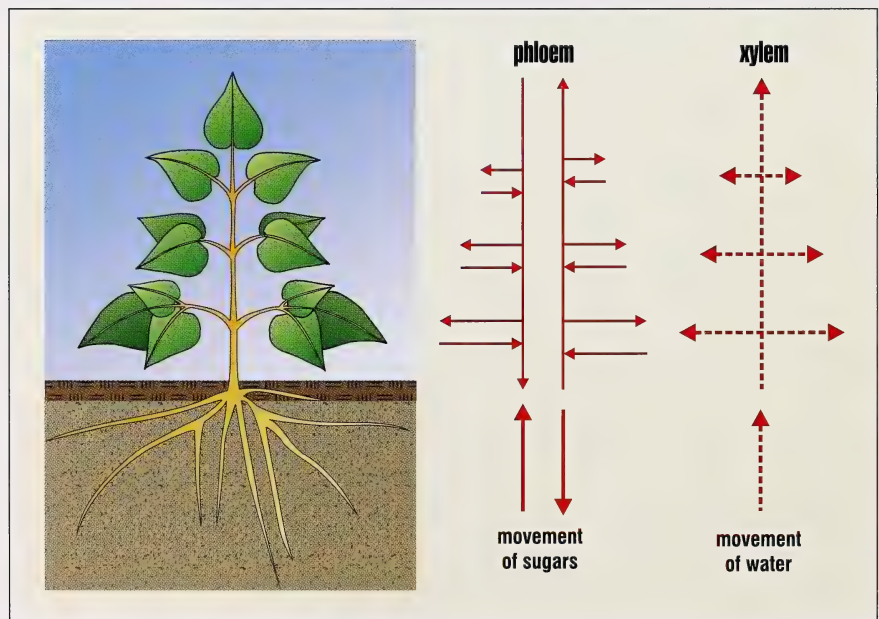
Figure 4. Herbicides can move in phloem and xylem, the two transport systems in plants.

The second transport system is the phloem, which moves solutions both up and down in the plant. Phloem sap moves in living cells, unlike xylem flow which moves through dead cells. Thus, the plant has more control of phloem transport than xylem. Phloem is the primary sugar transport system. During the growing season, sugars move from the leaves, where they are made, to the balance of the plant where they are used as an energy source. Perennial weeds move sugars up from the roots during spring growth and down after flowering to store them for next year's growth. Phloem also moves amino acids, the building blocks of proteins, within the plant.

Herbicides move passively in the phloem, but to do so, they must enter living cells. Herbicides that move well in the phloem are those that readily enter living cells (as described previously). They may have intermediate solubility and/or be weak-acid herbicides.

Why is translocation of interest? Frequently, perennial weed control depends on the herbicide killing roots and rhizomes at a considerable distance from the leaves where the herbicide is applied. If the herbicide translocates, long-term perennial weed control can be achieved. If not, top growth is removed while roots and rhizomes are unaffected; thus, long-term control will not be achieved.

Both physical/chemical properties of solubility and weak acid nature affect translocation (Figure 5). For example, the dinitroanalines (Group 3) are hydrophobic and tend to remain in the oily and waxy parts of the plant and not move readily. The ALS inhibiting herbicides (Group 2) are more likely to move in phloem and can thus be applied to the foliage, move through the plant and control distal roots in perennial weeds.
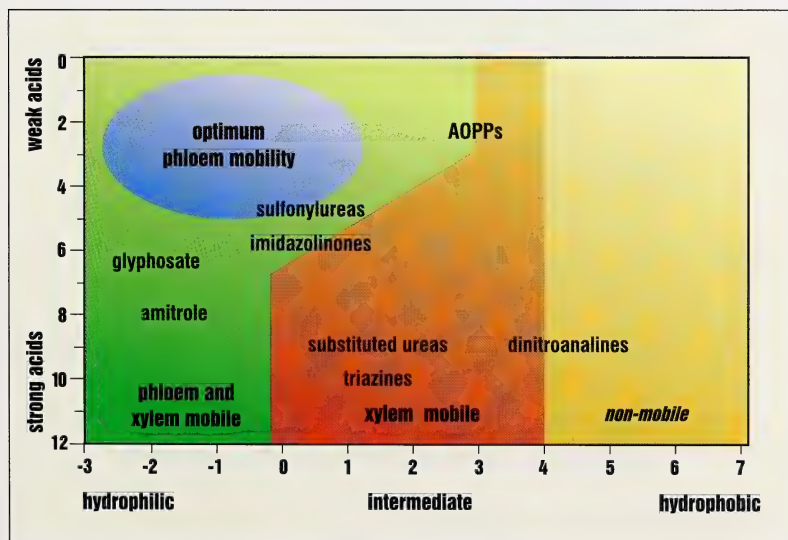
Figure 5. The influence of solubility and acid nature of common herbicides on translocation in both phloem and xylem.

Selectivity and metabolism

Some herbicides, like glyphosate (Roundup), are not selective. They affect most plants. Other herbicides, such as metsulfuron methyl (Ally), are selective. They do not affect cereal crops, but kill many broad-leaved weeds.

Selectivity usually depends on the crop's ability to break down or metabolize the herbicide more rapidly than the weed (Figure 6). Following metabolism, herbicides are frequently joined (conjugated) to sugars or amino acids. It is believed that these forms of the herbicide are non-toxic and move to the cell vacuole. Analogous to this action is the ability of humans to metabolize caffeine. Caffeine is quite toxic, but humans can degrade it rapidly to reduce its toxic effects (Figure 7). A major exception to metabolism as a selectivity mechanism is the Group 1 herbicides applied on broad-leaved crops (see Inhibitors of ACCase).

Many herbicides, such as diclofop-methyl (Hoegrass), are formulated as **proherbicides**. Proherbicides are generally able to penetrate the cuticle that covers foliage. Once in the plant, the plant changes them into the herbicidally-active form. In the case of diclofop-methyl, the methyl group is removed by an enzyme, and diclofop (the active molecule) is formed.
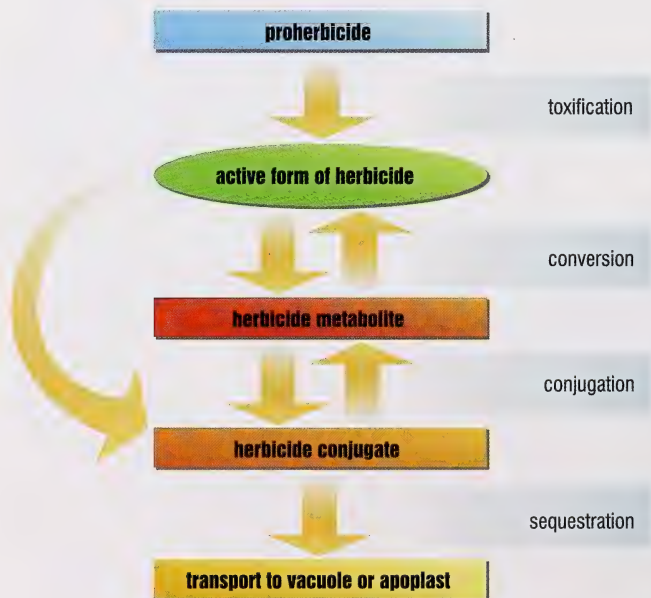
Figure 6. Most herbicides are chemically altered by the plant.
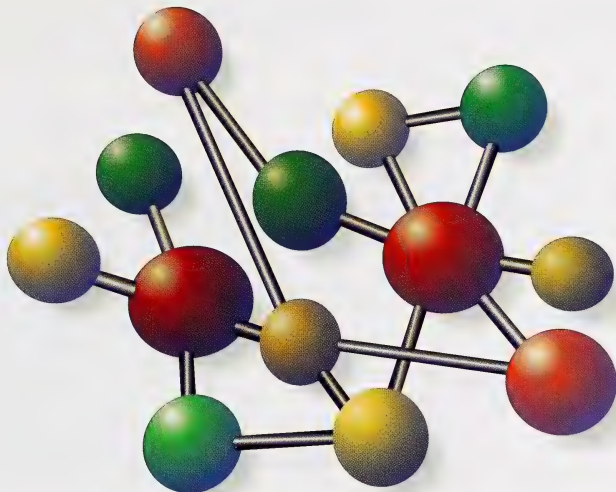
Figure 7. Herbicides, like all chemicals, are toxic at some dosage.

Toxicity

One way to determine non-target toxicity is through feeding studies. Rats (or other mammals and fish) are fed herbicides at various doses, and the percentage killed is measured. The dose that kills one-half of the subjects is called the LD_{50} (Lethal Dose for 50 per cent of the population) (Figure 8).

Figure 8. Oral toxicity of herbicides is measured and an LD_{50} is determined.

Oral toxicity is only one measure of risk, food chain effects and environmental impact. An in-depth discussion of toxicity is beyond the scope of this publication, but the LD_{50} gives a quick measure of relative oral toxicity. LD_{50}s and other toxicological information are available in the *Herbicide Handbook*.

LD_{50} of some common chemicals

Compound	LD_{50} (mg/kg rat body weight)	Toxicity
Glyphosate (Roundup)	5,600	Least
Imazethapyr (Pursuit)	>5,000	⇓
Table salt	3,000	⇓
Vitamin A	2,000	⇓
Diclofop (Hoegrass)	580	⇓
Nicotine	53	Most

Soil-Applied Herbicides

- can have variable activity and residue levels
- may require incorporation to reduce volatilization and photo degradation
- are degraded by soil microbes
- are degraded more rapidly under warm, moist conditions

Herbicides applied to soil are subjected to many physical and biological processes that can make it difficult to predict efficacy levels and residue (Figure 9).

Herbicide interaction with soil varies with the following:

- herbicide characteristics
- the soil type, pH and organic matter and
- available soil moisture

The interactions are both variable and unpredictable. Herbicides differ in the tenacity with which they bind to soil and organic material. For example, ethalfluralin (Edge) adheres more tightly to organic matter than to clay particles. Ethalfluralin bound to
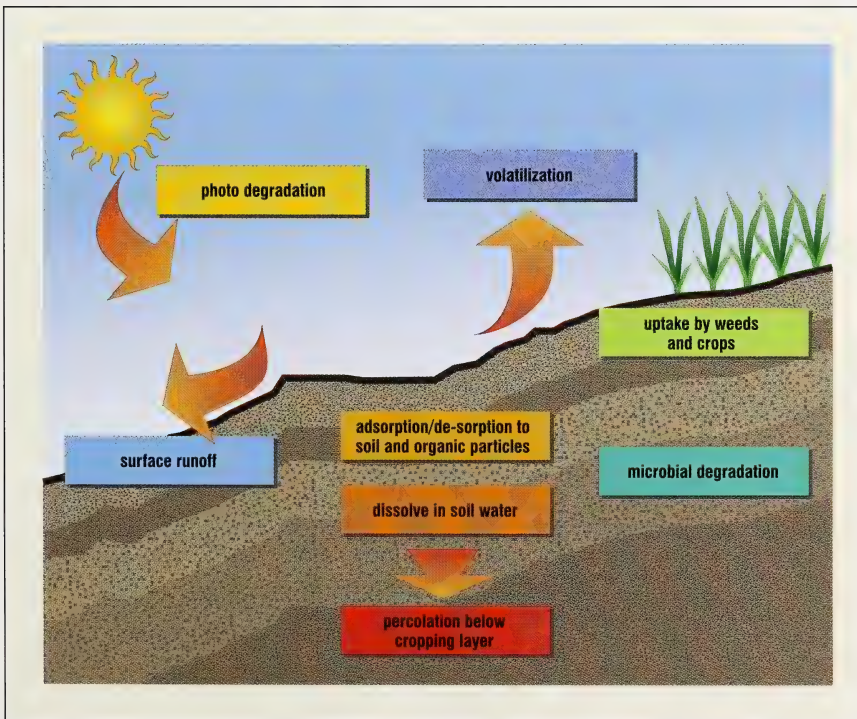
Figure 9. Many physical and biological processes affect herbicides in soil.

organic matter is not available to control weeds. Therefore, as the organic matter content of the soil increases, the application rate of a herbicide needed for weed control also increases.

Some herbicides may bind so closely to soil that they are unavailable for uptake by plants. Some bind so loosely they can be subject to movement in soil water, moving with surface runoff and moving up and down through the soil profile. Herbicides specifically applied to the soil bind moderately tightly to soil constituents and have little potential for leaching into surface and ground water.

The breakdown of herbicide residues depends on soil microbial activity, which can vary with soil temperature, soil moisture and the fertility of the soil. In conditions where the degradation of herbicide residues is slow, the crops that follow later in the rotation can be damaged.

Many soil herbicides require incorporation, which can aid in several ways. Incorporation can mix the herbicide and soil, distributing it evenly and at the optimum depth for activity. It can also reduce herbicide loss due to volatilization and photo degradation.

Inhibitors of Cell Division

- affect roots more than shoots
- cause affected plants to have stubby, pruned roots
- are applied at higher rates on high organic matter soils
- are incorporated to prevent volatilization and photo degradation

In Alberta, the dinitroanalines (DNAs) (Group 3) are commonly used for grass and broad-leaved weed control in canola, cereal and legume crops. DNAs are pre-emergence, soil-applied herbicides which act by inhibiting cell division and elongation.

Trade and common names for dinitroanaline herbicides

Class	Common name	Trade names
Dinitroanaline	trifluralin	Advance 10G
		Bonanza
		Heritage
		Rival
		Treflan
		Trifluralin 10G
		Trifluralin 400
	ethalfluralin	Edge

Physical/chemical properties

Trifluralin (Treflan) and ethalfluralin (Edge) are bright yellow (Figure 10). They were originally investigated by chemical manufacturers for use as dyes.

Both herbicides are poorly soluble in water but readily soluble in organic solvents. They can be formulated as emulsifiable concentrates to be applied in a water carrier or as granules. They are not weak-acid herbicides; therefore, solubility in soil water and efficacy do **not** change with the pH of the soil.

Trifluralin and ethalfluralin are slightly volatile. Their volatility increases in wet soil. They bind more tightly to organic matter than to clay particles. Tightly bound herbicides are unavailable to control weeds. Therefore, in soils of high organic content, higher rates of herbicide may be required. This result is more apparent for ethalfluralin than trifluralin. Both herbicides are degraded by sunlight, especially during warm days.

DNAs are commonly incorporated to reduce losses due to volatilization and photo degradation as well as to position the herbicide in the soil (see below).

Because these herbicides are strongly adsorbed by soil, they have low leaching potential.

Microbial action in the soil is responsible for degradation of DNAs. Herbicide residues can be a concern in following crops during cool or dry conditions.
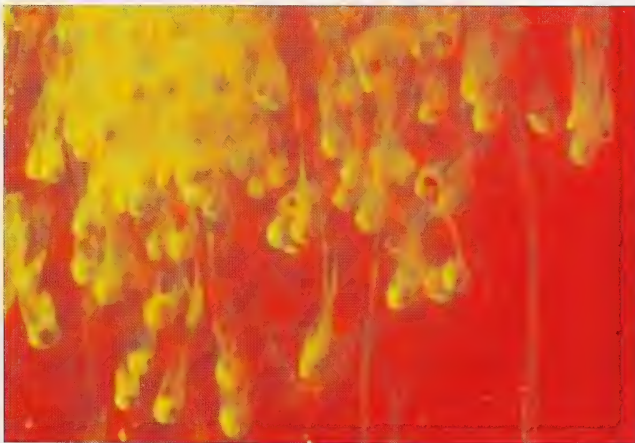
Figure 10. Edge granules are bright yellow.

Inhibition of cell division and cell enlargement

Trifluralin and ethalfluralin inhibit cell division in plants by inhibiting the synthesis of the protein "ropes" that pull the chromosomes apart during cell division.

Cell division is essential for plant growth. During normal cell division, chromosomes double and are then pulled apart into two cells (Figure 11).

The small "ropes" that pull apart and separate the chromosomes are called microtubule fibres. They are made up of the protein tubulin and are constantly being made at one end of the cell and taken apart at the other end (treadmill synthesis) (Figure 12).

The dinitroanalines bind to the microtubules in the place of tubulin and stop further fibre synthesis. Degradation, however, continues. Consequently tubules get shorter, not longer, and soon there are no tubules to pull apart the chromosomes. Cell division is interrupted, and "aberrant" cells are created (Figure 13). When cell division is disrupted:

- chromosomes do not line up and separate
- nuclei replicate extensively
- a cell wall does not form
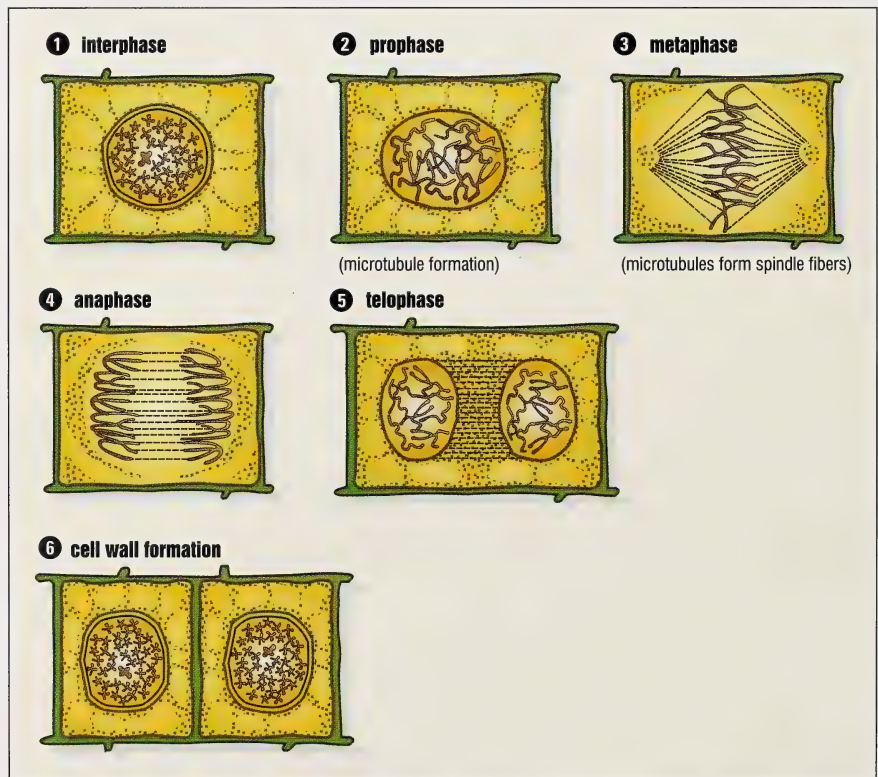
Figure 11. A normal cell division during which microtubules separate duplicate chromosomes and align the plate where the new cell wall forms.
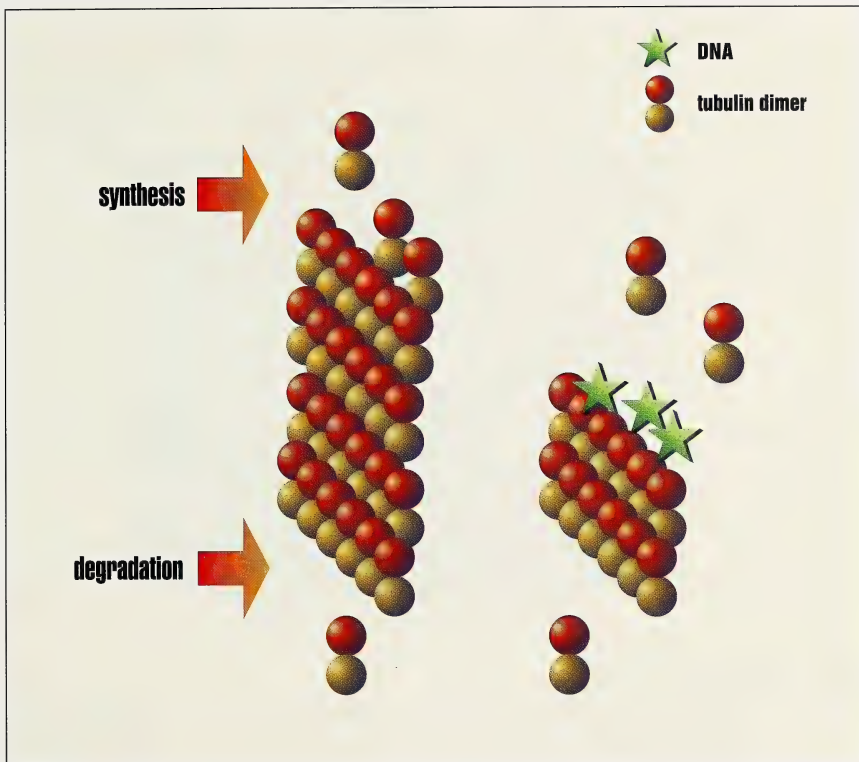
Figure 12. Treadmill synthesis of microtubules. Both synthesis and degradation happen simultaneously. By changing the rate of synthesis and degradation, the length of the tubules changes. Dinitroanaline herbicides bind in the place of tubulin dimers, stopping synthesis. Because degradation continues, the fibres become short and non-functional.
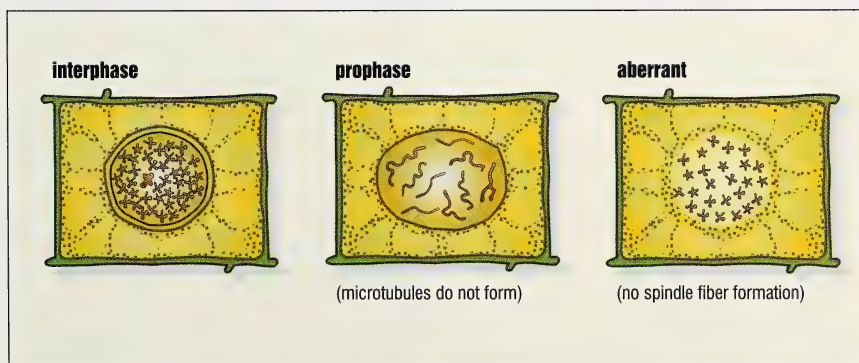
Figure 13. When dinitroanaline herbicides are present, cells do not divide and aberrant cells form.

The DNAs affect plants and regions of plants that are rapidly growing and dividing. Cell division occurs primarily in the meristematic regions of the plant. Root meristems are located in root tips and in lateral buds along the sides of the roots. In grasses, the root meristems are at the coleoptilar node (base of the coleoptile) where secondary root growth is initiated. Shoot meristems in broad-leaved weeds and crops are located at the base of the cotyledons. In grasses, the shoot meristem is the crown, located above the base of the coleoptile, wrapped inside developing leaves.

If DNAs come into contact with rapidly growing parts of the plant, they inhibit cell division. Symptoms are apparent when cell division is occurring rapidly.

Uptake and translocation

DNA binding to soil limits movement into plants. It has been speculated that DNAs may enter plants in a vapor state. Seedlings intercept DNAs as they grow through the treated-soil layer. DNAs are presumed to dissolve readily into the lipid-based membranes of seedlings.

There is thought to be little translocation of DNAs following uptake. Therefore, unless DNAs enter a meristematic region, and enter the nucleus of a cell, they can have little effect.

Metabolism and selectivity

Selectivity in DNAs is **not** based on metabolism. The selectivity of DNAs is unique and is based on several factors, including the following:

- the inability of these herbicides to translocate
- depth of incorporation
- their highly lipophilic (oil-loving) nature and
- the differing positions of weed and crop meristems

Trifluralin and ethalfluralin have little or no effect when applied directly to foliage.

Selectivity between grass weeds and cereal crops – Primary roots and the coleoptile node (or crown) are important sites of DNA activity in cereal crops and grass weeds. While the position of the primary root is the same, the position of the coleoptile node differs among wheat and barley and some grass weeds (wild oat and green foxtail).

Wild oat and green foxtail exhibit mesocotyl elongation, which pushes the coleoptile upward (Figure 14, 15). Wheat and barley do not. Mesocotyl elongation of grass weeds pushes the DNA-sensitive coleoptile node through the DNA-bearing soil layer. The DNAs enter the coleoptile node and inhibit cell division, eventually leading to plant death. Wheat and barley also grow through the DNA-treated layer, but expose only the coleoptile, which is not sensitive to inhibition.

Selectivity between broad-leaved weeds and crops – Selectivity among broad-leaved weeds and crops is less well understood. There is a reported correlation between the ability of the plant to tolerate DNAs and the oil content of seeds. The highly hydrophobic DNAs may dissolve in the lipid fraction of these seeds and thus not reach the site of action.
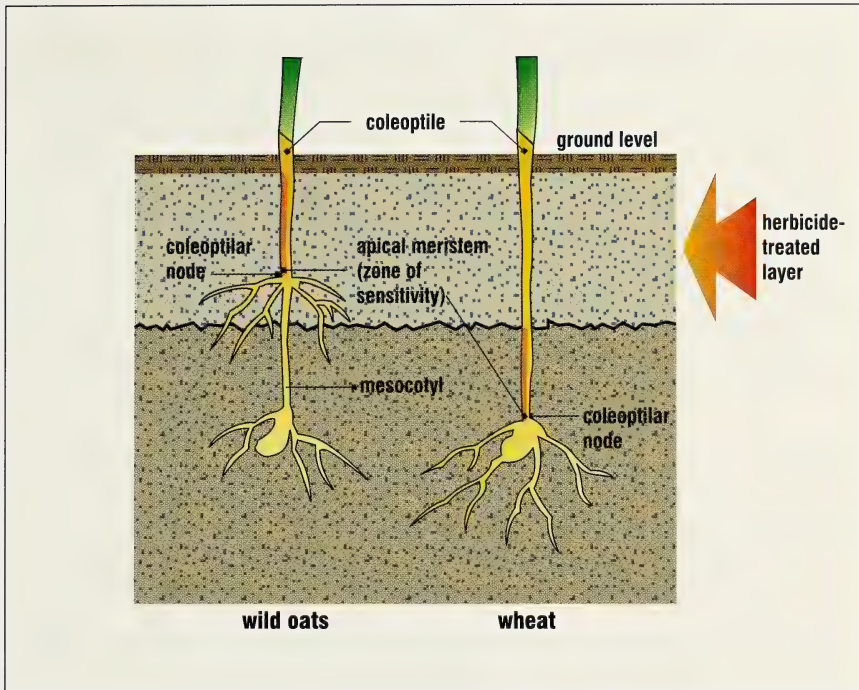
Figure 14. Different growth patterns in wild oats and wheat contribute to selectivity. Wild oats exhibit elongation, which pushes the zone of sensitivity into the herbicide-treated layer. Wheat does not exhibit elongation.

Photo: Beth Hoar

Figure 15. Growth patterns in wild oats and wheat. Note the position of the zone of sensitivity, where secondary roots have formed.

Symptoms

DNAs stop the growth of root tips and cause root tip swelling as cells enlarge without longitudinal cell growth. Shoot elongation is inhibited, the hypocotyl of dicots thickens and stems enlarge. A successful DNA application is characterized by little weed emergence. The seedlings that do emerge show root pruning and stubby root tips (Figure 16).

Toxicity

DNAs have no effect on mitosis of most animal cells. They are non-hazardous to birds, but trifluralin added directly to water is toxic to fish. The strong adsorption to soil and the soil application method minimize potential hazards to fish. However, runoff from fields directly into ponds should be avoided.

Trifluralin has a high LD in rats (10,000 mg/kg body weight) and other mammals, indicating low oral toxicity. Chronic toxicity is low.

Implications for application

- Depth of incorporation and depth of seeding are critical to the success of DNA herbicides.
- DNAs are strongly adsorbed to soil organic matter. Soils with high organic matter or with heavy crop residues often require higher rates.
- DNAs should be incorporated to reduce losses by volatilization and photodecomposition and to correctly position the herbicide for maximum efficacy.
- There is little risk of leaching.
- These herbicides are relatively safe to handle.

Figure 16. Severe damage by Edge on wheat showing stubby roots but also some shoot damage, which occurs only at very high rates.

Surface-applied Edge

Edge has had limited applicability for farmers in direct seeding. This situation may be changing.

Edge applied to the soil surface without incorporation may soon be registered for fields that have been in direct seeding for three years.

Farmers who have already tried surface application of Edge are apparently pleased with its performance. How does surface application of Edge work?

Direct-seeded fields differ in several ways from tilled fields. There is increased organic matter (crop residue) on the soil surface. Weed seeds germinate mostly on the surface of the soil in direct seeding, not from below the organic layer as they would in fields in which tillage is conventional.

When Edge is surface-applied, a concentrated zone of herbicide is placed where weed seeds germinate. Although binding to organic matter, volatilization and photo degradation will increase where Edge is surface-applied without incorporation; the concentration of herbicide in the tip layer along with the weed seeds apparently compensates for losses and inactivation.

Inhibitors of Very Long Chain Fatty Acid Biosynthesis

- soil applied
- must be incorporated
- placement at the correct soil depth is critical for selective control
- affected weeds fail to emerge
- affects shoots more than roots

The thiocarbamates (Group 8) are also soil-applied herbicides but differ in many ways from the DNAs. Although these herbicides have been used for many years, not much is known about how they work. While placed here with the dinitroanalines, the other major soil-applied herbicides, they may be more appropriately compared to the other inhibitors of fatty acid biosynthesis, the ACCase inhibitors.

Physical/chemical properties

Thiocarbamates are liquid in their unformulated states and vary in solubility. Triallate (Avadex) is the least water soluble followed by butylate (Sutan) and EPTC (Eptam). The reverse relationship exists for organic solvents. Triallate is soluble in most organic solvents, while butylate and EPTC are only miscible. They are not weak acids.

Once applied to soil, triallate adsorbs to soil colloids, while butylate and EPTC are less tightly held. Thiocarbamates can be volatilized from soil at high temperatures or from wet soil, unless incorporated.

Formulation can also play a role in the amount of volatilization and, thus, the amount of incorporation necessary. For example, the liquid formulation of Avadex is more susceptible to volatilization loss and must therefore be incorporated quickly following application. On the other hand, the granular formulation incorporation can be completed within 48 hours of application, followed by a second incorporation in 3 to 5 days. The liquid formulation binds tightly to crop residues and should only be used where soil is exposed and crop residues are low. The granular formulation can be applied to fields with high levels of crop residue.

Like the DNAs, microbial degradation is responsible for the degradation of thiocarbamates in soil. Degradation is rapid under most conditions, but under dry conditions, wheat grown in the following year can be affected. For Avadex, the only re-cropping restriction on the label is to an oat crop in the following year.

Note:
While difenzoquat (Avenge 200C) is also in Group 8, it has a different mode of action, which has never been fully explained.

Trade and common names for thiocarbamate herbicides

Class	Common name	Trade names
Thiocarbamates	triallate	Avadex BW
		Fortress*
	EPTC	Eptam
		Eradicane 8-E
	butylate	Sutan*

* contained in a mix

Inhibition of very long chain fatty acids (VLCFA)

Thiocarbamates inhibit an enzyme in fatty acid biosynthesis that elongates fatty acids to form waxes and suberin (Figure 17). Both these compounds are important in maintaining a waxy layer on the outside of seedlings and in preventing water loss.

While it is known that herbicides inhibit VLCFA biosynthesis and that cell elongation and division are inhibited, the physiological link between them is unclear. Even though these herbicides have been used successfully for many years, the way in which they work to control weeds is still unknown.

Uptake and translocation

Thiocarbamates enter grass weeds through the coleoptile and coleoptile node as it pushes through the treated soil.

Translocation is not essential to the function of these herbicides. Triallate tends to dissolve in the lipid fraction of seeds and seedlings, while EPTC and butylate move through the soil solution and then into seedlings more readily.

The limited translocation of thiocarbamates occurs primarily in xylem and corresponds to their water solubility. Triallate has poor translocation, while EPTC (Eptam) and butylate are translocated more readily.
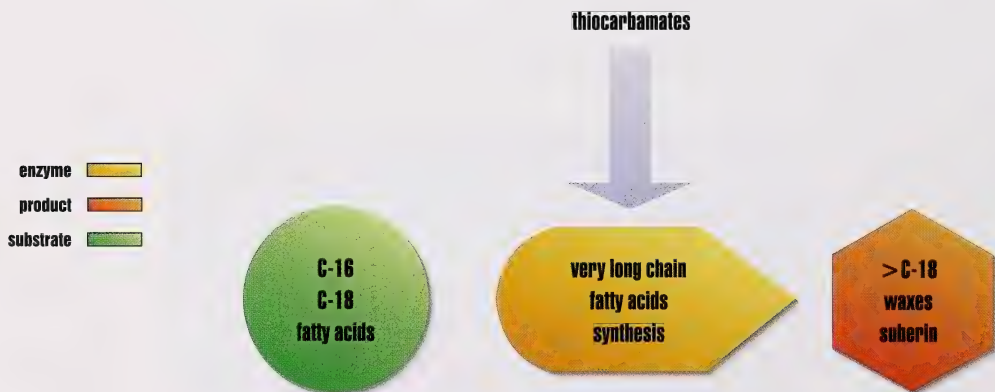
Figure 17. The thiocarbamates inhibit the synthesis of very long chain fatty acids (carbon chain length greater than 18) and block production of waxes and suberin.

Metabolism and selectivity

Selectivity between grassy weeds and grass crops depends on the position of the crop relative to the herbicide-treated soil layer. Cereal crops must be placed below the herbicide layer, lest they absorb the herbicide and be affected.

Selectivity in crops and broad-leaved weeds varies. While butylate and EPTC control some broad-leaved weeds, triallate has no activity on broad-leaved weeds. The reasons for this lack of activity are unknown.

Thiocarbamates are metabolized in plants, but it is unclear what role metabolism plays in conferring selectivity.

Toxicity

Thiocarbamates have low oral and dermal mammalian toxicity.

Symptoms

Affected grassy weeds frequently fail to emerge. Cell elongation in the shoots slows dramatically. Shoots, if they emerge, often appear swollen and bright green. Shoots often emerge from the sides of the coleoptile and can form a loop (Figure 18).

Unlike the DNAs, thiocarbamates affect shoots more than roots. The thiocarbamates may induce abnormal emergence of the first leaf from the coleoptile. Coleoptile growth is inhibited. Leaves may appear darker green. While plants treated with DNA may also fail to emerge, roots are often pruned, leaving stubby root knobs.
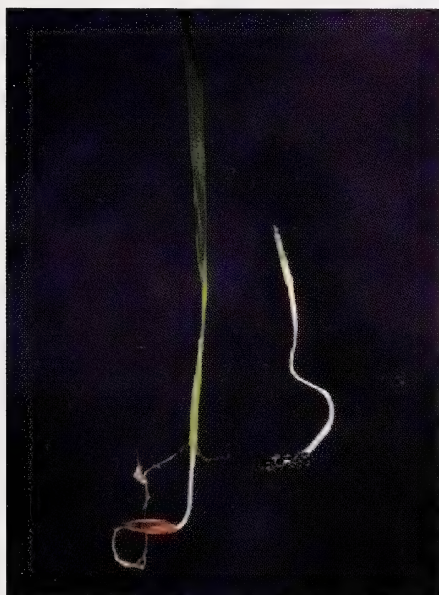
Photo: Beth Hoar

Figure 18. Avadex symptoms on wild oats showing inhibited shoot growth.

Implications for application

- Thiocarbamates must be incorporated to position the herbicide in the layer of soil containing weed seeds and to reduce losses due to volatilization.
- Cereal crops must be planted below the layer containing herbicide.
- Persistence in soil is relatively short due to losses by volatilization and microbial degradation.
- Mammalian oral toxicity is low.

Amino Acid Biosynthesis Inhibitors

- the most widely used herbicides in the world fall into this class
- affect amino acid and therefore protein synthesis in plants
- symptoms vary from type to type

Several types of herbicides affect amino acid synthesis, and each inhibits a different enzyme. Three will be discussed in detail (Figure 19):

- ALS inhibitors, the Group 2 herbicides like Ally and Assert;
- EPSPS inhibitors, glyphosate (Roundup) (Group 9), and
- inhibitors of glutamine synthetase, glufosinate ammonium, sold as Liberty and included in Roundup Fast Forward (Group 10).
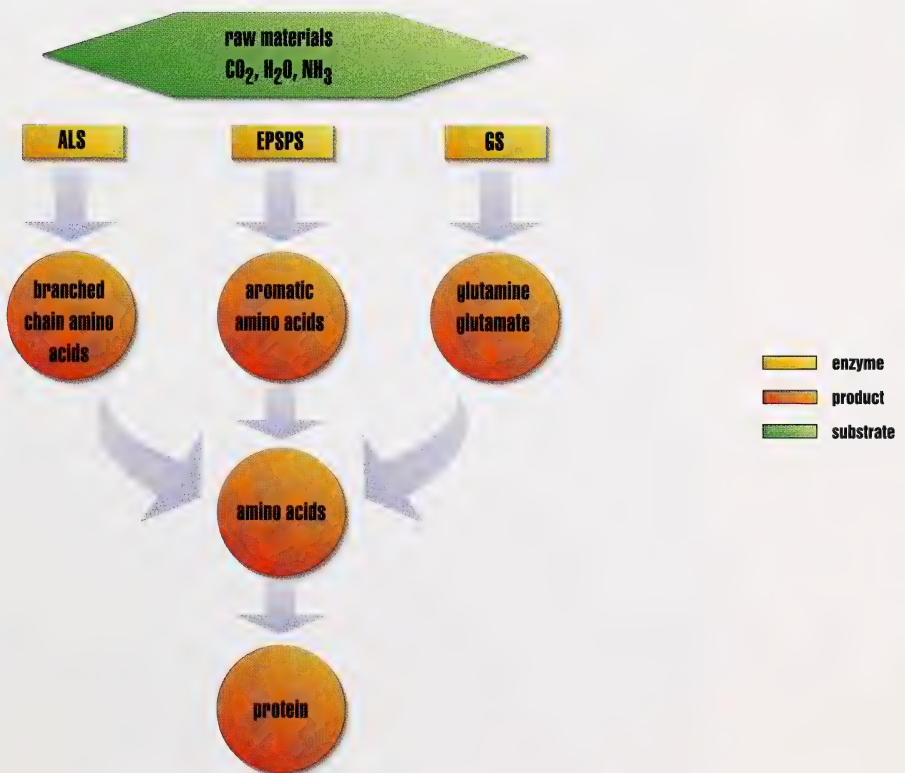
Figure 19. Three different groups of herbicides inhibit amino acid biosynthesis.

Amino acids are the building blocks of proteins. Proteins are critical to the function of all biological organisms. As enzymes, proteins function as catalysts, which direct and accelerate biochemical reactions. Some proteins assist with the transport of components throughout the plant, while others serve as nitrogen and energy storage compounds.

Plants manufacture all essential amino acids, while mammals, including humans, have a limited ability to synthesize amino acids. Therefore, a chemical that inhibits the synthesis of amino acids in plants is toxic to plants, but is less likely to find a target in animals. To date, most amino acid biosynthesis inhibitors have very low mammalian toxicity.

Inhibitors of Acetolactate Synthase (ALS)

- selective herbicides that can affect both broad-leaved and grass herbicides
- soil active
- soil persistence varies but can limit rotational options
- moves readily throughout the plant
- plant death is slow
- not toxic to mammals

Trade and common names for sulfonylurea (SU) and imidazolinone (IM) herbicides

Class	Common names	Trade names
Sulfonylaminocarbonyl-triazolinones	flucarbazone-sodium	
Sulfonylurea	chlorsulfuron	Telar
	ethametsulfuron methyl	Muster, Muster Gold*, Muster Gold II*
	metsulfuron methyl	Ally, Escort
	nicosulfuron	Accent
	rimsulfuron	Prism
	sulfosulfuron	Anthem*, Sundance
	thifensulfuron methyl	Champion Extra*, Champion Plus*, Freedom Gold*, Harmony Total*, Laser DF*, Muster Gold*, Refine Extra*, Triumph Plus*
	triasulfuron	Amber, Unity*
	tribenuron methyl	Crossfire*, Express Pack, Refine Extra*
Imidazolinones	imazamethabenz	Assert 300
	imazamox	Odyssey*
	imazethapyr	Odyssey*, Pursuit

* contained in a mixture

Two classes or families of herbicides inhibit the same enzyme target site. While their chemical structures are different, the way in which they affect plants is indistinguishable.

Physical/chemical properties

Sulfonylureas and imidazolinones are weak-acid herbicides with intermediate water solubility. As such, they are readily taken up by leaves and roots and transported in both the phloem and xylem (see uptake and translocation).

Soil persistence of the sulfonylurea and imidazolinone herbicides varies with soil conditions such as organic matter, pH, soil moisture and temperature. Soil adsorption increases as organic matter increases. As soil microbes are required for degradation, warm wet soils enhance breakdown. The response to soil pH differs between sulfonylureas and imidazolinones. As pH decreases, sulfonylurea persistence decreases. With imidazolinones, persistence increases as soil pH decreases.

Because these herbicides are soil active and because some crop species such as canola, sunflower and sugar beet are **very** sensitive to them, herbicide residues in soil are a concern (Figure 20). As a result, one of the most persistent of the sulfonylureas, chlorsulfuron (Glean, Telar) is no longer marketed for crops. Crop rotation restrictions apply to many of the sulfonylurea and imidazolinone herbicides. Check herbicide labels for further information.

Photo: David Wall
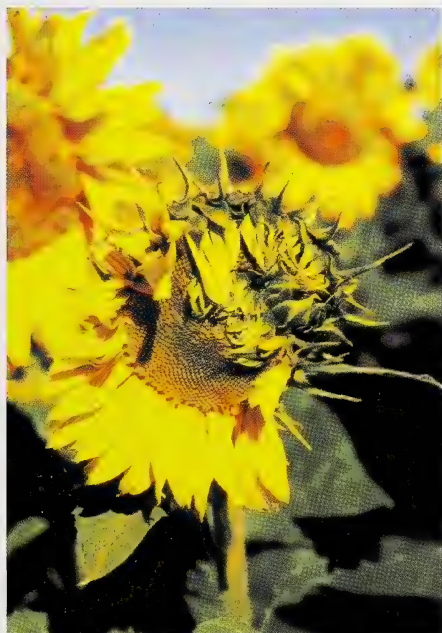
Figure 20. Damage to sunflowers caused by Pursuit residue.

Inhibition of acetolactate synthase (ALS)

ALS is a key enzyme in the synthesis of branched-chain amino acids (Figure 21). It synthesizes two reactions, the condensation of two molecules of pyruvate to form an acetolactate and the condensation of a molecule of pyruvate with one of αketobutyrate to form acetohydroxybutyrate. This dual action has resulted in two names being used for the same enzyme, acetolactate synthase (ALS) and acetohydroxy acid synthase (AHAS).

ALS is located in the chloroplasts of green tissue and the plastids of non-green tissue. ALS is most active and, therefore, most sensitive to inhibition in young meristematic regions of plants.
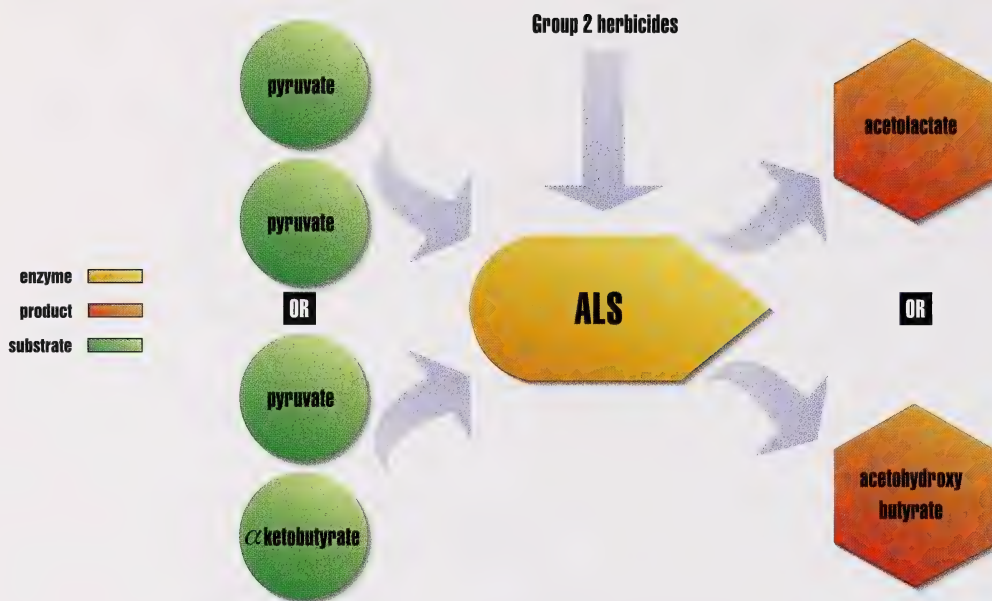
Figure 21. All Group 2 herbicides inhibit acetolactate synthase (ALS). Enzyme inhibition leads to an accumulation of α ketobutyrate, a reduction in protein synthesis and eventually to plant death.

Both the SUs and IM herbicides bind to and inhibit ALS. Inhibition of this enzyme leads to reduced amounts of the branched-chain amino acids: leucine, valine and isoleucine. However, plant death is not only due to starvation for these amino acids. Following herbicide application, cell division is inhibited. There may be a build-up of the toxic intermediate α ketobutyrate and a decrease in the phloem translocation. The initial inhibition apparently causes a cascade of events that eventually kills susceptible plants.

Uptake and translocation

ALS inhibitors, while usually foliar-applied, can have soil activity. Thus, these herbicides may persist in the soil and affect newly germinating weeds in addition to those weeds that received a foliar application.

Foliar-applied herbicides are taken up readily by the plant and translocated in the xylem and phloem. They are also readily taken up from the soil and can move in both xylem and phloem.

It should be noted that these chemicals have almost a perfect chemical profile for translocation, a result of their intermediate permeability and weak acid nature. These factors, along with low adsorption to soil, result in soil activity. However, one component of their activity is inhibition of phloem transport. Thus, they tend to inhibit their own movement. While these herbicides translocate well, they are less mobile than Group 4 herbicides, like clopyralid (Lontrel).

Metabolism and selectivity

All ALS inhibitors used in crops are selective; they control the weed without affecting the crop.

Selectivity is based on the ability of crop plants to rapidly metabolize these ALS-inhibiting herbicides before they become toxic. Weeds are controlled because they metabolize these herbicides at a slower rate.

One reason for the widespread use of these herbicides is that ALS inhibitors have a broad spectrum of selectivity and flexibility of use. For example, the herbicide ethametsulfuron methyl (Muster) is selective enough to remove wild mustard from canola crops.

Soil persistence with these herbicides varies because of the rate of herbicide degradation in the soil. For example, microbial activity degrades tribenuron methyl and thifensulfuron (Refine Extra) more quickly than metsulfuron methyl (Ally). Thus, metsulfuron methyl remains in the soil longer, increasing weed control but also increasing the residual effects on sensitive crops.

Toxicity

Branched-chain amino acids are not synthesized by mammals; therefore, the ALS enzyme is not present in mammals. The sulfonylureas and imidazolinones generally have few toxicological concerns.

Symptoms

The first visible symptom is an inhibition of plant growth in susceptible species. A few days after application, chlorosis followed by necrosis and terminal bud death are visible. Yellow and purple coloration may appear on leaves and stems (Figure 22, 23). Root growth can also be inhibited. Plant death is relatively slow.

Photo: Beth Hoar

Figure 22. Symptoms of Ally on stork's-bill.

Photo: Beth Hoar

Figure 23. Symptoms of Muster on wild mustard.

Implications for application

- ALS herbicides are active at very low rates.
- They are active both as a foliar application and following uptake from the soil.
- Selectivity conferred by differential metabolism allows use with a wide range of crops and target weeds.
- Soil activity, persistence in the soil and extreme sensitivity of some crops impose rotation restrictions.
- ALS herbicides have very low acute mammalian toxicity.

Inhibitor of EPSPS

- non-selective herbicide
- effective on most broad-leaved and grass weeds and crops
- translocates readily through plants
- provides good perennial weed control at higher rates
- no soil activity because it binds tightly to soil and is inactivated

Glyphosate, sold as Roundup, Touchdown or Glyfos, is one of the best known herbicides in the world. It is non-selective, foliar active and perceived as one of the safest herbicides available (Figure 24).

Figure 24. Canola varieties tolerant to amino acid biosynthesis inhibitors, including Pursuit/Odyssey/Refine, Roundup or Liberty, are widely grown across the Canadian prairies.

Trade and common names for glyphosate

Class	Common name	Trade names
	glyphosate	Roundup, Roundup Transorb
		Glyfos, Laredo
		Wrangler
		Renegade
		Round-up Fast Forward*, Rustler*, Touchdown

* contained in a mixture

Physical/chemical properties

Glyphosate (Roundup), formulated as an isopropyl amine salt, is highly water soluble but not soluble in organic solvents. It is not volatile. Recently, a different formulation of glyphosate, a trimethylsulfonium salt rather than an isopropyl amine salt, has been registered under the trade name of Touchdown.

Glyphosate is a weak acid but is unusual in that it loses not one but several protons, at different pH optimums. As such, it is called a zwitterion.

Glyphosate is strongly bound to clay particles in the soil. Once glyphosate is bound to soil, it is unavailable to plants. Residual activity and leaching are thus negligible.

Glyphosate is a weak acid that can be 'trapped' in a cell. In addition, it may be carried across the plasma membrane by a phosphate carrier, a protein located in the plasma membrane that normally moves phosphate.

Inhibition of EPSPS

Glyphosate binds to and inhibits the enzyme 5-enolpyruvylshikimate acid-3-phosphate synthase (EPSPS), an enzyme in the aromatic amino acid biosynthetic pathway (Figure 25). As in the case of ALS inhibitors, phytotoxicity does not result from starvation for amino acids. Inhibition leads to deregulation of carbon flow in the plant and a build-up of the toxic intermediates, shikimate or shikimate-3-phosphate.
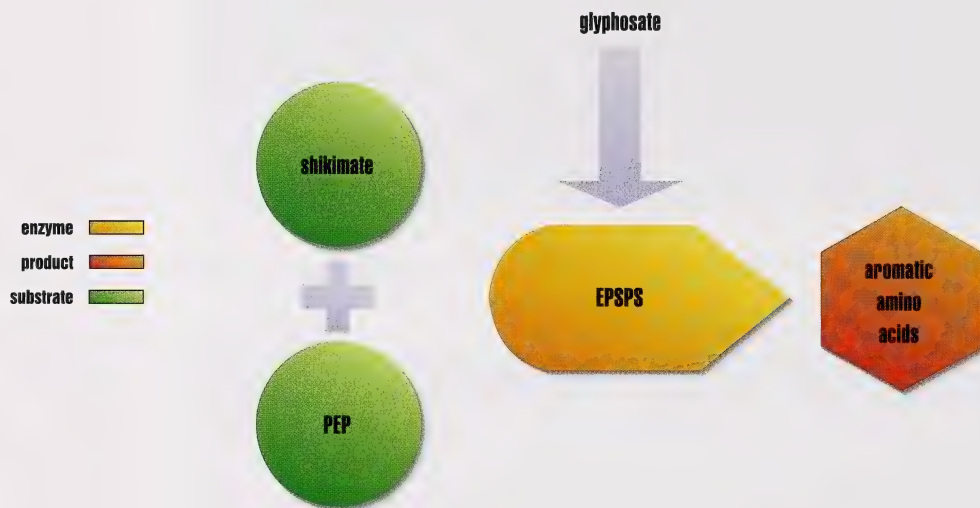
Figure 25. Glyphosate inhibits a key enzyme in aromatic amino acid biosynthesis.

Uptake and translocation

Glyphosate is taken up readily from the foliage, although movement through lipid layers may be slow. Like many herbicides, the formulation of the product will affect the rate of uptake and thus rain fastness. Additionally, surfactants influence uptake (see chapter on Adjuvants).

The translocation of glyphosate is adequate in phloem and xylem, but like ALS inhibitors, it is not as good as expected from its chemical profile. Glyphosate alters the carbon balance in treated plants, which reduces carbon flow to sugar, the transport molecule in phloem. If sugar is not pumped into phloem, then phloem transport in general is depressed, trapping glyphosate in the leaves. Like ALS inhibitors, glyphosate seems to inhibit its own movement in phloem (Figure 26). Translocation can be maximized by timing application during a period when perennials are moving sugars downward, after flowering for most plants.

Glyphosate moves with the sugars in growing plants. When it is applied as a crop desiccant too early, when seed moisture levels are too high, it can move to seeds as they are forming. Glyphosate in seeds can decrease germination and seedling vigor. Therefore, glyphosate may not be used on crops that will be used for seed production.
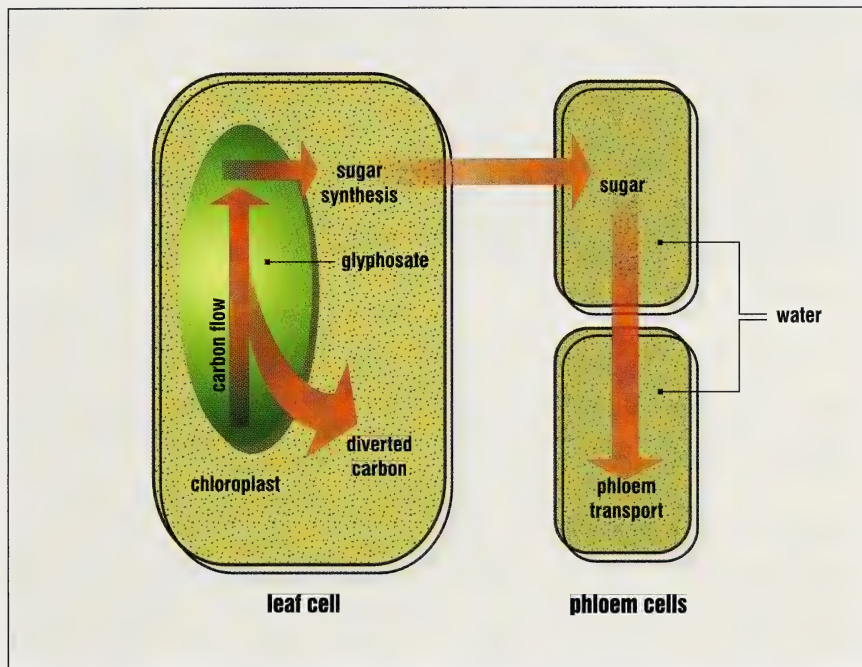
Figure 26. Glyphosate tends to inhibit its own movement in phloem by reducing sugar synthesis, which is essential to phloem transport.

Metabolism and selectivity

Glyphosate is a non-selective herbicide. Plants do not readily degrade glyphosate.

In the soil, degradation is accomplished by micro-organisms.

Although glyphosate is non-selective, considerable variability exists in the amount of herbicide necessary to control various weeds. Some weeds are remarkably hard to control with Roundup, like field horsetail or wild buckwheat. This difficulty may be because glyphosate cannot penetrate the waxy coating on the plant.

Symptoms

As with inhibitors of ALS, glyphosate symptoms are slow to appear. Symptoms are most apparent at the growing point of the plant. Leaves turn yellow, followed by browning (Figure 27). At sub-lethal rates, there can be some twisting of the plants that might be confused with 2,4-D symptoms.
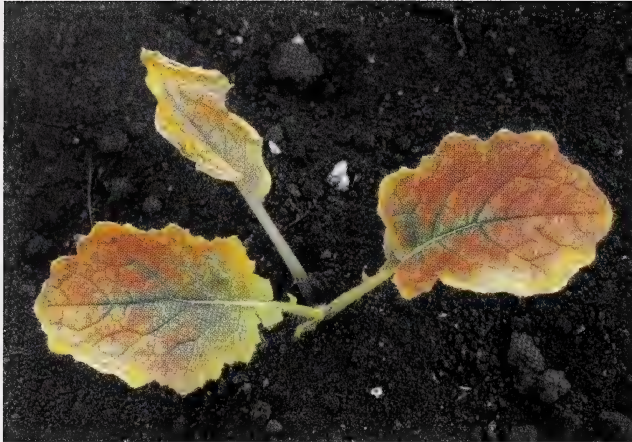
Figure 27. Roundup symptoms on canola.

Toxicity

Glyphosate binds to an enzyme not present in humans and is non-toxic to use. It has low oral and dermal toxicity. Because glyphosate is formulated as a salt, it can irritate the eyes.

Implications for application

- Glyphosate binding to soil inactivates it, allowing seedlings that germinate after application to survive.
- Glyphosate does not leach from soil.
- It has very low mammalian toxicity.
- Perennial weed control depends on translocation to distal roots and rhizomes.
- Glyphosate can be inactivated in the spray tank if water containing dirt or organic matter is used.

Inhibitor of Glutamine Synthetase

- non-selective, contact-type herbicide
- symptoms include the appearance of grey-white patches that appear rapidly
- poor perennial weed control

A single herbicide has been commercialized from this chemical class. It is non-selective.

Trade and common names for glufosinate

Class	Common name	Trade name
	glufosinate ammonium	Liberty, Roundup Fast Forward

Physical/chemical properties

Glufosinate (Liberty) is highly water soluble and is a weak acid. It is not volatile.

Glufosinate adsorbs only weakly to soil and can be highly mobile. However, glufosinate breaks down rapidly by soil microbial action and, thus, has limited soil persistence and limited potential for leaching. This herbicide was originally discovered in a bacterium species, but it is now manufactured synthetically.

Inhibition of glutamine synthetase

Glufosinate binds to glutamine synthetase (GS), a key enzyme in the pathway that assimilates inorganic nitrogen (ammonia) into useful organic compounds (Figure 28). In addition to the assimilation of ammonia, GS recycles ammonia produced by other metabolic pathways, including degradation of storage and transport protein and photorespiration.

Glufosinate binds to GS in the binding site normally occupied by glutamate. Binding is irreversible. The measurable symptoms following application are rapid accumulation of ammonia, rapid drop in photosynthesis, depletion of amino acids, glutamine, glutamate and others, growth inhibition, chlorosis and plant death.

Initially, it was proposed that death was caused by the accumulation of ammonia. It has been subsequently determined that this accumulation alone does not cause death. It has been shown that glyoxylate, an inhibitor of RUBISCO, a key enzyme in the 'dark' reactions of photosynthesis, accumulates following herbicide application. It has been proposed that symptoms are due to the blockage of photosynthesis and subsequent production of toxic oxygen radicals (see Photosynthetic Inhibitors chapter). The threads of the story are still unraveling.
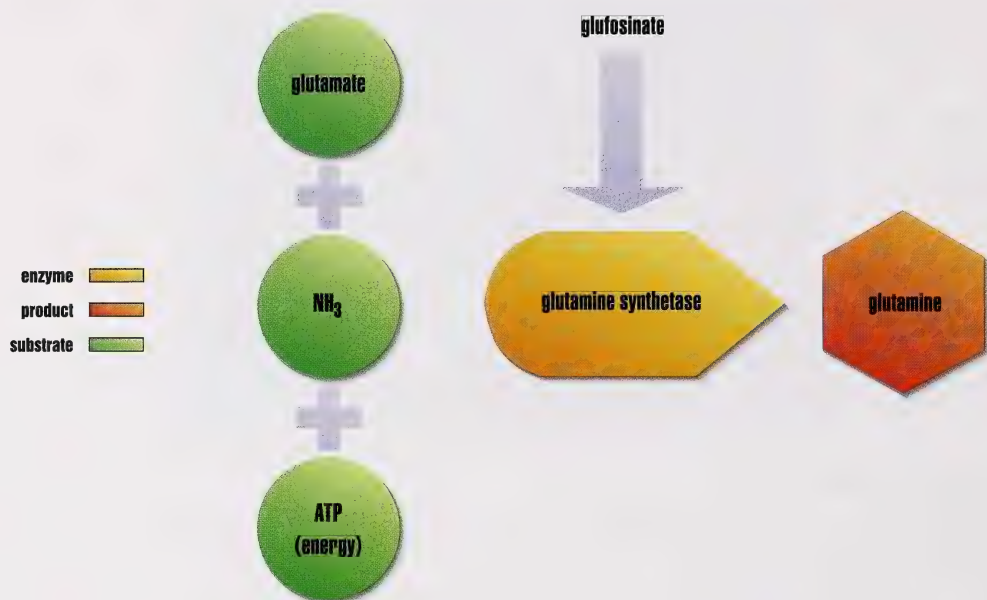
Figure 28. Glufosinate inhibits glutamine synthetase, an enzyme that combines in organic NH_3 with glutamate to form glutamine.

Uptake and translocation

Glufosinate is very water soluable and is a weak acid. As such, it should translocate well in both phloem and xylem. Translocation is limited because the rapid activity of the herbicide quickly disrupts photosynthesis and cell integrity. This herbicide effectively limits its own translocation.

Metabolism and selectivity

Although glufosinate is a non-selective herbicide, considerable variability in species sensitivity exists.

Glufosinate is metabolized in plants, but not quickly enough to avoid toxic consequences. Tolerance in "Liberty Link" canola has been conferred by the insertion of the 'PAT' gene, isolated from bacteria, which increases the rate of metabolic degradation.

Toxicity

Glufosinate has a low acute oral toxicity (2,270 mg/kg body weight male rats, 1,730 mg/kg body weight female rats) and is a mild skin irritant.

Symptoms

Chlorosis and wilting usually occur within one to three days of application, followed by necrosis in one week. Symptom development is more rapid in bright sunlight, high humidity and moist soil (Figure 29, 30).

Implications for application

- Because glufosinate is highly water soluble, it can be washed from leaves by rain for up to four hours following application.
- Seedlings that emerge following application are unaffected.

Figure 29. Liberty on wild mustard.

Figure 30. Liberty on wild mustard (detail).

Inhibitors of ACCase

- grass herbicides
- poor water solubility
- no residual soil activity
- do not move readily in the plant
- 'dims' degrade in the sunlight
- adjuvant choice is critical for 'dims' efficacy
- fops and dims used in broad-leaved crops cause virtually no crop damage
- selectivity in cereal crops is due to herbicide metabolism by the crop
- anything that delays herbicide breakdown, like poor growing conditions, can increase crop injury

ACCase Inhibitors

Commonly known as the 'fops' and 'dims,' ACCase inhibitors (Group 1) affect grasses but not broad-leaved weeds or crops. Some are selective, while others are effective on all grass species, both crops and weeds. The range of selectivity in these post-emergence herbicides along with their broad-leaved crop tolerance has made them some of the most useful herbicides for Canadian producers.

Trade and common names for fop and dim herbicides

Class	Common name	Trade names
Aryloxyphenoxy propionate (fops or AOPPs)	clodinafop-propargyl	Harmony Total*, Horizon, Platinum*
	diclofop-methyl	Hoe-Grass 284 Hoe-Grass II*
	fenoxaprop-p-ethyl	Champion Extra*, Champion Plus*, Fusion*, Laser DF*, Puma, Puma Super, Triumph Plus*
	fluazifop-p-butyl	Fusion*, Venture
	quizalofop-p-ethyl	Assure, Assure II, Freedom Gold, Muster Gold*, Muster Gold II
Cyclohexanedione (dims)	clethodim	Select
	sethoxydim	Poast Flaxmax*, Poast Ultra
	tralkoxydim	Achieve, Achieve Extra* Prevail*

* contained in a mixture

Physical/chemical properties

Two classes of chemistry, the 'fops' and the 'dims,' affect the same target site. They have important similarities and differences.

In general, both the fops and dims are poorly water soluble. With the exception of Venture and Achieve, they are all formulated as emulsifiable concentrates containing organic solvents to make them miscible with water. When you open a container of these herbicides, the organic solvent is what you smell, not the herbicide. While the fops, and at least some dims, are weak acids, their poor water solubility limits phloem mobility.

Neither the fops nor dims are volatile.

They are only active as a foliar spray and are **not** taken up from the soil solution. Therefore, there is no residual activity.

Degradation in the soil occurs by soil micro-organisms. All these compounds are degraded readily. Rapid degradation reduces leaching into ground and surface water.

Most dims degrade rapidly in sunlight (photo degraded). The herbicides are exposed to sunlight when on the surface of the leaf. If they degrade before entering the leaf, activity can be lost. This property has caused novel formulation concepts, including the use of sunscreen for herbicides. Formulations currently used for the dims are designed to hasten herbicide uptake by plants, thus reducing photo degradation. It is very important for these compounds to use the adjuvants recommended for the products. Substitution of adjuvants may lead to product failure (See Adjuvants chapter). Some research has indicated that these herbicides can be more active when applied at dusk rather than at dawn.

The fop herbicides are formulated as proherbicides, with a methyl, ethyl or butyl group attached. These methyl, ethyl or butyl groups make them even less soluble in water but better able to penetrate the waxy cuticle of plants. Once inside the plant, the methyl, ethyl or butyl groups are removed enzymatically, and the biologically active compound, i.e., diclofop or fenoxaprop, is formed.

The dims differ chemically from the fops. They are not applied as proherbicides and do not come in active and inactive forms.

Inhibition of ACCase

Both fops and dims are important in inhibiting an initial enzyme in the synthesis of fatty acids, acetyl co-enzyme A carboxylase (ACCase). Fatty acids are important components of membranes, like the cell membrane and the chloroplast membrane, that not only contain the cell fluids (cytosol), but also serve as a gateway to compounds entering and leaving the cell. Fatty acids are also used as building blocks for waxes and suberin for the cuticle and are used to store energy.

Some of the fop herbicides have a "**P**" in the center of the common name (fenoxaprop-p-ethyl). All the fops are chemically synthesized in two forms, which are mirror images of one another. Only one of these forms is herbicidally active. When the active form is chemically separated from the inactive form and then sold, the designation "**P**" is used.

Fops and dims bind to and inhibit ACCase of grass plants, slowing down and stopping fatty acid synthesis. This action halts membrane synthesis, which is necessary for cell growth and synthesis (Figure 31).

The enzyme ACCase is a very large, complex molecule that uses energy to add a simple carbon compound, bicarbonate, onto a carbon chain. The carbon chain is held by a metabolic handle (Coenzyme A). Both the fops and dims bind to the same enzyme, but it is unclear where on the enzyme the binding site is located. It is believed that binding and inhibition occur during the final stage of the enzyme action, during the transfer of the bicarbonate to the carbon chain, rather than during the initial binding of substrates or ATP (the energy carrier).

ACCase is located primarily in chloroplasts and is active in young, growing meristematic tissues. In grass crops and weeds, ACCase activity is highest at the base of young, growing leaves and at the crown region. The fops and dims must reach this area to be effective. It is also here that herbicide symptoms are first visible. Inhibition of ACCase causes growth in the meristem to slow or stop.

When seedlings are growing quickly, there is a great demand for membrane building material. It is during rapid growth that ACCase is most active and, therefore, also when these inhibitors are most effective. When growth is slowed by drought or plants are more mature, the inhibitors are less effective.

Figure 31. Group 1 herbicides inhibit the enzyme ACCase, critical to the formation of fatty acids.

Uptake and translocation

These hydrophobic herbicides penetrate the cuticle and enter leaves quite readily. Uptake of the dims is assisted by special adjuvants. Using the correct adjuvant is critical to the efficacy of the 'dims,' Achieve, Poast and Select.

Once inside the leaf, both fops and dims are translocated relatively slowly to the meristem, where ACCase is located. The meristem of grasses is in the base of the leaves and crown.

Herbicide spray coverage is important to increase the efficacy of these herbicides. Grass morphology can aid. Droplets tend to run down the grass leaves, placing the herbicides where they can be more effective. For more detail, see the Dose Transfer chapter.

While translocation of fops and dims is much slower than glyphosate or ALS inhibitors, phloem mobility can be sufficient to control quackgrass and other perennial grasses. Those herbicides that translocate most readily are more effective on perennial weeds in which the herbicide must reach distal root and rhizome tissue.

Metabolism and selectivity

Selectivity between broad-leaved crops and grass weeds – The fops and dims do not inhibit ACCase from broad-leaved crops and weeds (with a few exceptions). This insensitive target site makes broad-leaved crop tolerance to the fops and dims very high.

Selectivity between cereal crops and grass weeds – Selectivity between cereal crops and grass weeds depends on the rapid metabolism of the herbicide by the crop and the relatively slower metabolism in the weed. Cereal crops such as wheat have high levels of enzyme-mediated metabolism. Wheat degrades selective fops and dims very quickly, limiting potential damage. In wild oat and other grass weeds, metabolism is much slower, allowing the herbicide to reach and inhibit the sensitive ACCase. The metabolism of fops and dims is highest in the youngest crop plants. Growing conditions that limit herbicide metabolism, such as drought and cold temperatures, can decrease crop tolerance. Transient effects on the crop include yellowing and slowed growth.

The crop selectivity of some fop herbicides can be enhanced by an additive that increases herbicide metabolism in the crop. The herbicides Puma Super and Triumph Plus contain the same active ingredient, fenoxaprop-p-ethyl. In Puma Super, fenoxaprop-p-ethyl metabolism in the crops is increased by the addition of mefenpyr diethyl to the herbicide formulation. Another strategy is to add MCPA and/or a sulfonylurea (thifensulfuron) to the formulation (Triumph Plus). The addition of MCPA (an auxin-like herbicide, Group 4) and thifensulfuron (Group 2) makes the fenoxaprop-p-ethyl safer on the crop and increases the number of weeds controlled. Therefore, Triumph Plus controls both grass and some broad-leaved weeds and is selective in wheat.

Herbicide mixtures and antagonisms – Because auxinic herbicides decrease the translocation and increase the metabolism of fop herbicides, tank mixing or subsequent application of fops and most 2,4-D-like herbicides can result in reduced grass herbicide efficacy. This effect can be overcome by increasing the dose of the grass herbicide. Check the labels for compatibility and application-delay intervals.

Toxicity

The oral (rat) LD_{50} of these products ranges from 550 mg/kg of body weight for diclofop-methyl (Hoegrass) through 1,630 for clethodim (Select) to 2,676 kg/mg body weight for sethoxydim (Poast). Specific toxicities can be found in the *Herbicide Handbook*.

Symptoms

Symptoms on grass weeds are relatively slow to appear because of the slow translocation of the fops and dims, and because inhibition of cell division is not immediately deadly (Figure 32, 33). Both root and shoot growth are inhibited. Wilting and chlorosis (yellowing) may be evident on leaves (Figure 34). This stage is followed by drying and necrosis of leaves. Affected grasses can be pulled easily from the soil, or leaves can be easily pulled from the crown. This effect is due to the "pinching" of the meristematic base of the seedling. This pinching is found only in the fops and dims. Pinching occurs at the base of the leaves because the ACCase enzyme is found primarily in the rapidly growing portion of the plant.

Photo: Beth Hoar

Figure 32. Group 1 herbicides cause meristem damage. Their leaves are easily pulled from the plant.

Figure 33. Damage to meristem (detail).

Figure 34. Group 1 herbicides also cause chlorotic spotting and stripping of grass leaves.

Water quality

If the 'dims' are applied in water with dissolved salts, like well water, the salts bind to the herbicide and inactivate it. Loss of activity results, seen most frequently under poor growing conditions or when rates are reduced. Ammonium sulfate added to the application solution prevents this loss of activity.

Implications for application

- Limited translocation suggests that adequate coverage, meaning the placement of the herbicide droplet close to the base of the seedling, is important for control.
- Tank mixing and sequential application of fop and broad-leaved herbicides must follow label directions.
- Application to broad-leaved crops is usually safe.
- There are no soil persistence problems with these compounds.
- Dim herbicides should be applied in water that contains few dissolved minerals or applied with liquid ammonium sulfate.

Auxinic Herbicides

Auxinic herbicides are effective on broad-leaved weeds.

* sold as an ester, amine or salt formulation
* formulation affects uptake by plants, rainfastness and water quality interactions
* auxinic herbicides are usually translocated very well
* they have some soil activity
* symptoms include abnormal and rapid growth

Herbicides that mimic the plant growth regulator known as auxin are some of the oldest and most trusted herbicides used in agriculture.

Trade and common names for the auxinic herbicides

Class	Common name	Formulation	Trade name(s)
Phenoxy or Phenoxyalkanoic acids	2,4-D	LV ester ± amine	2,4-D, Attain*, Champion Plus*, Dichloprop D*, DyCleer*, DyVel DS*, Estaprop*, Thumper*, Tordon 101*, Turboprop*, Weedone CB*
	2,4-DB	ester	Caliber 400, Cobutox 600 Embutox 625
	MCPA	amine ester K-salt Na-salt	MCPA, Achieve Extra*, Buctril M*, Champion Plus*, Curtail M*, DyVel*, Laser DF*, Mirage*, Platinum*, Poast Flaxmax*, Prestige*, Stampede CM*, Target*, Triumph Plus*, Tropotox*
	MCPB	salt	Tropotox*, Tropotox Plus*
	mecoprop	salt	Compitox, DyVel DS*, Mecoprop, Target*
Benzoic acid	clopyralid	salt	Curtail M*, Lontrel, Poast Flaxmax*, Prestige*, Prevail*, Transline
	dicamba	salt	Banvel, DyCleer*, DyVel*, DyVel DS*, Mirage*, Rustler*, Target*
	fluroxypyr	unknown	Attain*, Prestige*
	picloram	salt	Tordon 22K, Tordon 101*
	triclopyr	ester	Garlon, Fencerow, Tordon 202C*
Qumoline carboxylic acid	quinclorac	acid	Accord

± LV - low volatile
* contained in a mixture

Physical/chemical properties

Most auxinic herbicides are active in the acid form but are formulated as esters, amines and salts to enhance the ability of these herbicides to enter the plant. The exception is quinclorac (Accord), which is formulated as an acid.

Formulation differences are simply the addition of a "block" onto the herbicide molecule (Figure 35). The type of block added changes the chemical properties of the herbicide **outside** the plant.

Formulations affect the application and uptake of auxinic herbicides.

The ester form has some chemical advantages. Esters are not very water soluble, but dissolve readily in oil or organic solvents. Esters can be applied in water as emulsions with a suitable emulsifying agent. Ester forms may be used in relatively hard water. These forms also tend to resist washing from the leaves following a rain shower. The methyl, ethyl and isopropyl esters are no longer available because of their high volatility, which made them subject to vapor drift. New, low volatile esters have larger side chains that reduce their volatility. In general, the phytotoxicity of esters is higher than for amine or salt forms under difficult environmental conditions.

By contrast, amines and salts are very water soluble. Reduced weed control or sludge formation in the spray tank may occur with amine formulations applied in hard water, but most commercial mixtures contain inhibitors to prevent this problem. Additionally, some amine formulations can be incompatible with liquid fertilizer. The water solubility
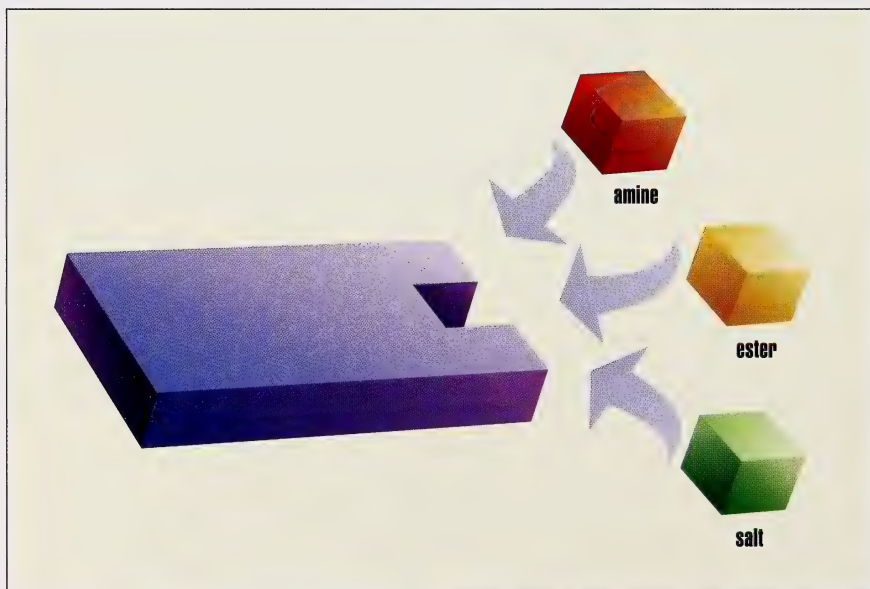
Figure 35. By adding a different 'block' to the herbicide, formulations can change factors such as the way the herbicide enters the plant, solubility and volatility. The blocks separate from the herbicide after it enters the plant.

of these formulations makes them more susceptible to being washed from leaves by rain, but plant roots absorb salt forms of auxinic herbicides more readily.

Formulated products are converted in the plant to the acid, which is the active form of the herbicide. The acid is a weak acid and can therefore be acid trapped, enhancing uptake and translocation.

In general, auxinic herbicides are reversibly bound to soil. Adsorption to soil increases with organic matter content. More water soluble formulations, such as salts and amines, are more likely to move in soil water. These herbicides have some soil activity and residual concerns, but most are rapidly degraded in soil.

Soil degradation depends on microbial activity.

De-regulation of growth

Because these herbicides mimic the plant growth regulator, indole acetic acid (IAA), or auxin in plants, it is necessary to review the function of auxin in plants to properly understand their mechanism of action.

Role of auxin in plants – Auxin is a plant growth regulator that controls cell enlargement, division and plant development through the plant life cycle.

While much remains to be unraveled about the workings of IAA, it is known that IAA binds to auxin binding proteins (ABPs) located in the following:

* the cell membrane
* the endoplasmic reticulum (an internal cellular membrane system)
* the cell nucleus and
* dissolved in the cytoplasm

The control on growth that IAA exerts is multi-functional. Changes induced by IAA cause rapid changes in cell elongation and both rapid and slow changes in gene expression (Figure 36). Auxins influence other growth regulators including cytokinins, abscisic acid and ethylene, a gas that functions as a plant growth regulator.

The concentration of IAA in plant cells regulates cell growth. However, plant tissues differ in their sensitivity. Depending on tissue type and IAA concentration, IAA may either inhibit or stimulate a response.

IAA is a component of a carefully balanced system (Figure 37). IAA concentrations are highly regulated in the plant by synthesis, degradation and both reversible and non-reversible conjugation. Synthesis increases the IAA content while degradation decreases it. Conjugation, which is the linking of IAA to another molecule, frequently an amino acid, inactivates IAA. However, if conjugation is reversible, it may act as a slow release mechanism for maintaining relatively constant IAA levels.

Auxin herbicide mode of action – Auxinic herbicides presumably bind to some or all of the same sites as naturally occurring IAA and cause similar effects. However, the amount of auxinic herbicides available to the plant is uncontrolled and, thus, auxin-like activity is unchecked. Plant growth becomes deregulated.
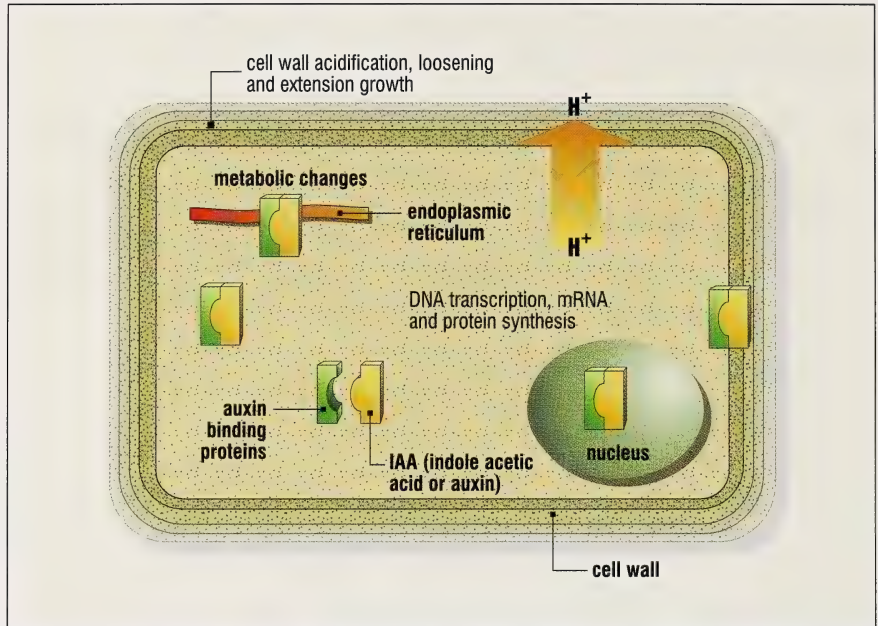
Figure 36. Auxin binding proteins have been identified in several locations: on the plasma membrane, dissolved in the cytoplasm and in the nucleus and endoplasmic reticulum (ER). Auxin binding causes a rapid efflux of protons, followed by cell wall loosening. Loosening of the bonds between the cell wall fibers allows the cell to increase in size. This action is called the 'acid growth phase'. Slower responses include enzyme induction, nuclear transcription, mRNA and protein and polysaccharide synthesis.
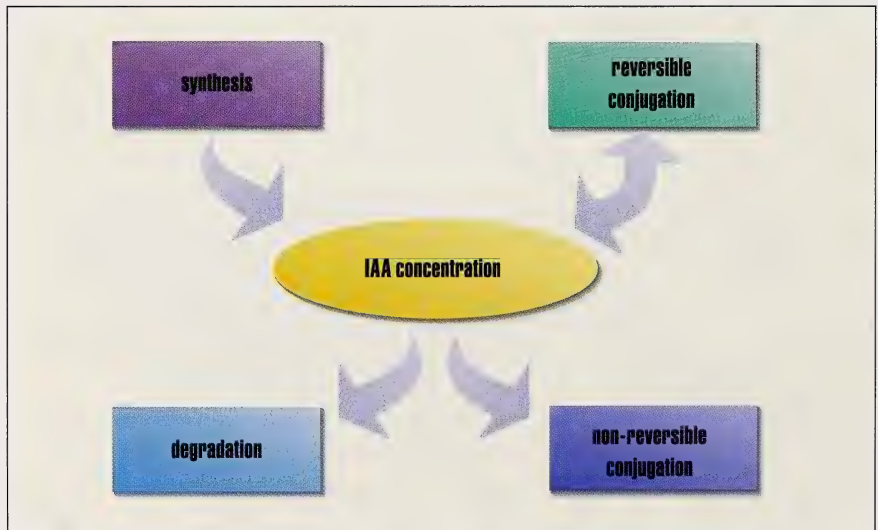
Figure 37. IAA concentration in plants is carefully controlled.

Metabolic reserves are mobilized and transported to the site of growth, usually meristematic regions. Unregulated growth leads to twisting, thickening and elongation of leaves and stems. Auxinic herbicides are active primarily in growing plants. Plant death is slow, due to the unconstrained mobilization of reserves, the breakdown of repair mechanisms and finally, the loss of function.

Quinclorac

Quinclorac is a selective herbicide that controls both grass weeds, including barnyard grass and green foxtail, and broad-leaved weeds, including cleavers. Quinclorac has both similarities and differences when compared with other auxinic herbicides.

In sensitive grasses, a rapid increase in ethylene has been measured. The levels of cyanide, an inhibitor of respiration, CO_2 and nitrate assimilates also increase. Cyanide is a by-product of ethylene biosynthesis (Figure 38). It has been shown that 2,4-D (and, by inference, other auxinic herbicides) also produces ethylene and cyanide. It has been suggested that cyanide may also contribute to death in sensitive grasses.
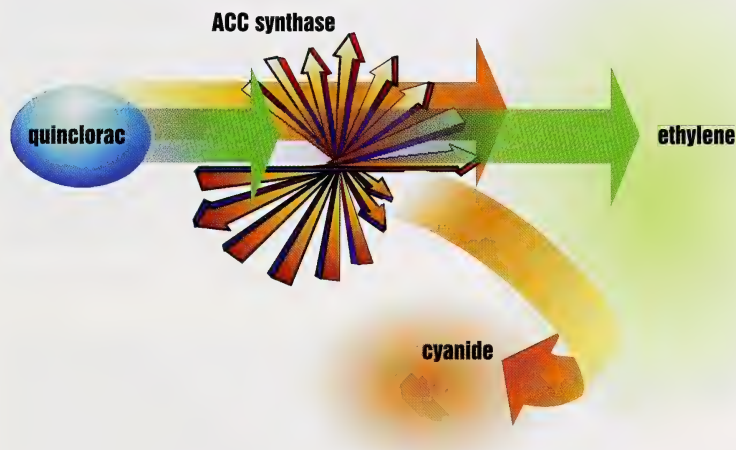
Figure 38. A secondary effect of quinclorac has recently been identified in grass weeds. In the presence of quinclorac, the enzyme ACC synthase increases activity, producing a large increase in ethylene, up to 60 times the normal amount. A by-product of ethylene biosynthesis is cyanide, a metabolic inhibitor.

Uptake and translocation

Auxinic herbicides move into plants following foliar application, primarily through leaves or stems. The ester formulation increases the rate of uptake of these compounds through the cuticle of leaves. Amine and salt formulations are absorbed more slowly and can be more easily washed from the leaves by rain. Herbicides vary in the uptake

from the soil, depending on water solubility, binding to organic matter in the soil and the rate of degradation in the soil. Amine and salt formulations are more easily taken up by roots than are ester forms.

One of the best qualities of these herbicides is their ability to translocate both upwards to the leaves and downwards to the roots. This ability to translocate allows activity on perennial weeds.

Auxinic herbicides are translocated primarily in the phloem. Because translocation direction and speed vary with the season in perennial weeds, spring movement is primarily upward while in fall, it is downward, herbicide translocation ability also changes. They probably enter the phloem in two ways:

- Auxinic herbicides are weak acids. There is a pH differential between the inside and the outside of cells, and the differential solubility of the protonated and unprotonated forms allows these herbicides to be "trapped" inside the cell and available to move into the phloem (See How Herbicides Work, Chapter 1).
- Alternately, these herbicides may bind to the auxin binding protein on cell membranes, which transport the herbicides into the cell.

Regardless, auxinic herbicides, once in the living part of the plant, move into phloem along with sugars and amino acids, moving toward the site of storage or new cell growth. They accumulate at the meristems, affecting growth.

Metabolism and selectivity

Cereals are tolerant to most auxinic herbicides. Tolerance differences between grasses and broad-leaved plants are due to morphological differences, the rate of herbicide translocation and metabolism. In broad-leaved plants, the auxinic herbicides cause phloem to be crushed, due to cell proliferation around the phloem. In grasses, the phloem is scattered and surrounded by protective fibres. Auxin herbicide movement is more restricted in grasses. In addition, grasses tend to degrade auxinic herbicides or metabolize them irreversibly. In broad-leaves, auxinic herbicide degradation is slow, and conjugation is primarily reversible. Therefore, in susceptible broad-leaves, the concentration of herbicide remains at toxic levels long enough to impair or kill the plant.

The plant's ability to degrade the herbicide determines, for the most part, differences in tolerance between broad-leaved plants.

In soil, auxinic herbicides are degraded by micro-organisms. The half-life in the soil varies with the herbicide as well as with environmental conditions. Soil conditions that favor rapid microbial growth also favor a rapid breakdown of auxinic herbicides.

A special mention must be made of 2,4-DB, which can be used in seedling alfalfa, Alsike and white clover. These broad-leaved plants are normally affected by 2,4-D. 2,4-DB is a proherbicide, that is, 2,4-D with an extra substitution. In itself, 2,4-DB is not toxic; however, most plants except legumes remove the substitution, converting 2,4-DB to

2,4-D. Legumes are not susceptible to 2,4-DB because they do not convert it to the toxic 2,4-D. This is one of the few herbicides that can be used in seedling alfalfa to control broad-leaved weeds.

Symptoms

Symptoms include epinastic bending and twisting of stems and petioles, stem swelling, especially at nodes, elongation, leaf cupping and leaf curling (Figure 39, 40). Leaf shape and venation often appear abnormal. These signs are followed by chlorosis at the growing point, growth inhibition, wilting and necrosis. Death of susceptible plants occurs slowly, usually within three to five weeks. At low concentration, young leaves may appear puckered, and the tips of new leaves may develop into narrow extensions of the midrib.

Photo: Beth Hoar

Figure 39. Symptoms of Attain on wild buckwheat.

Photo: Beth Hoar

Figure 40. Quinclorac can cause deformation of plant growth and development.

Toxicity

The following table shows acute toxicity (oral) of auxinic herbicides. The higher the number, the less toxic the compound.

Common name	Trade name(s)	LD$_{50}$ (male rats mg/kg)
2,4-D	2,4-D, Attain*, Champion Plus*, Dycleer*, Estaprop*, Thumper*, Tordon 202C*, Turboprop*	764
2,4-DB	Caliber 400, Cobutox 600, Embutox 625	1960
MCPA	MCPA, Achieve Extra* , Buctril M*, Champion Plus*, Dyvel*, Laser*, Laser DF*, Mirage*, Poast Flaxmax* , Stampede CM*, Target*, Triumph Plus*, Tropotox*	1160
MCPB	Tropotox*	680
mecoprop	Compitox, Mecoprop	650 (mouse)
dicamba	Banvel, Dycleer*	1707
clopyralid	Curtail*, Lontrel, Poast Flaxmax*, Prevail*	4300
triclopyr	Garlon	713
picloram	Tordon 22K	>5000
fluroxypyr	Attain*	unknown

* contained in a mixture

Implications for application

- Ester formulations should be used if water has high levels of dissolved salts.
- Ester formulations are more rainfast than amines and salts.
- Esters usually have slightly higher activity.
- Auxinic herbicides have good ability to translocate and can be effective on perennial broad-leaved weeds. Translocation ability is enhanced if herbicides are applied following bud initiation of perennial weeds.
- Residual soil activity is limited by rapid microbial degradation.

Mixing of auxinic herbicides and ACCase inhibitors
When applied together, Group 4 herbicides can neutralize some grass herbicides. The reason for this antagonism is not very clear. Check the label before applying these types of herbicides together.

Photosynthetic Inhibitors

- include both selective and non-selective herbicides
- include widely used herbicides such as atrazine, bromoxynil and metribuzin
- are poorly translocated in the phloem
- vary in soil activity
- usually work best under sunny conditions

Photosynthesis is the process by which plants convert light into chemical energy. This chemical energy is used to make carbohydrates from carbon dioxide and water. Photosynthesis is an ideal target for herbicides because only plants can photosynthesize.

Four groups of herbicides inhibit photosynthesis. Three affect the PS II site (Groups 5, 6 and 7), and one affects a site called PS I (Group 22). The two photosynthesis sites are both part of the 'light reactions,' the component of photosynthesis that harvests light and converts it to chemical energy. The PS II and PS I sites are found in two distinct locations in the chloroplasts. Electrons come first through PS II and then to PS I.

Photosynthesis

Understanding the activity of photosynthesis inhibitors requires a knowledge of chloroplast structure and the function of light reactions in photosynthesis.

Chloroplasts are organelles that carry out photosynthesis within the cells of plants (Figure 41). They are membrane pouches that enclose another membrane system,
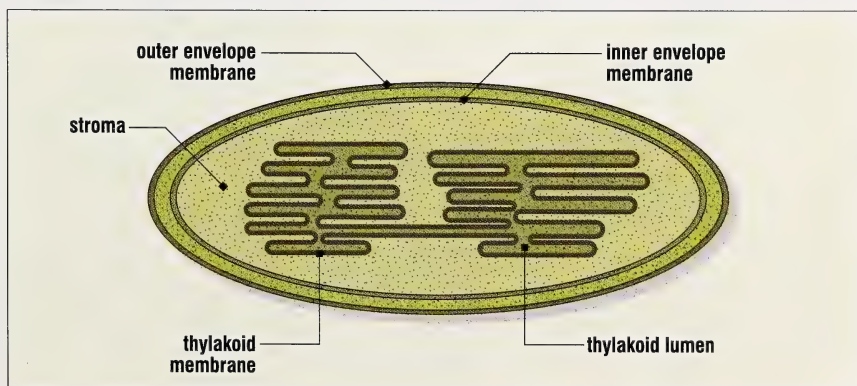
Figure 41. The chloroplast is an organelle found in plant cells. It is the site of photosynthesis. Chlorophyll is located in the thylakoid membrane.

called the thylakoid membranes. The thylakoids are folded and flattened membrane sacks. Fluids inside these sacks (thylakoid lumen) and outside (stroma) contain enzymes that are involved with the 'dark' reactions of photosynthesis and biosynthesis, including amino acid synthesis.

The product of light reactions, ATP and NADPH, are used to drive the fixation of CO_2, the formation of carbohydrates and thus all energy-requiring processes in plant cells (Figure 42).
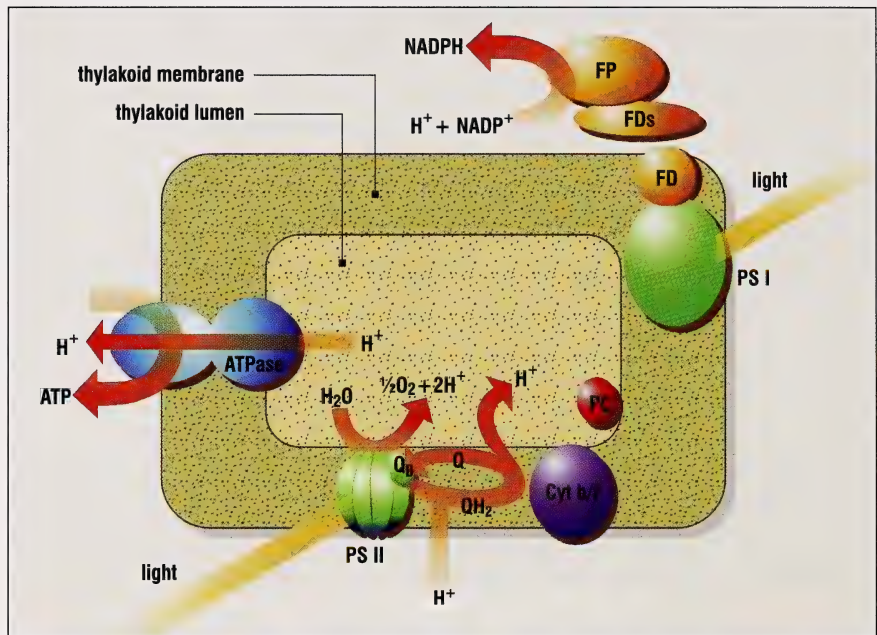
Figure 42. The light reactions of photosynthesis require movement of electrons from PS II, through Q_B, to Cytochrome b/f, to a plastiquinone (PC) then finally through PS I and several iron containing carriers, FD, FDs and FP. Electron movement transports protons, leading to ATP production, synthesizes NADPH and creates oxygen as a by-product.

PS II function

The first chlorophyll/protein complex involved in photosynthesis is PS II. It consists of chlorophyll antennae molecules and four membrane spanning proteins, which are associated with several electron accepting co-factors.

The PS II complex collects light using the chlorophyll antennae and then shifts this energy to an electron, which is boosted to a higher energy level. The lost electron is replaced by an electron extracted from water. Oxygen is a by-product of this reaction. Without the oxygen produced by plants, animal life is not possible.

The high energy electron is transferred to a series of electron acceptors, including Q_B. Q_B is a mobile electron carrier. Within the thylakoid membrane, Q_B docks by binding to one of the protein strands (called the Q_B binding protein). There, Q_B accepts first one, and then a second electron. When the second electron is accepted, Q_B un-docks and diffuses through the membrane towards the cytochrome acceptor chain, Cyt b/f and PC. In its place, another Q_B docks to accept the next series of electrons.

The movement of Q_B powers the transfer of protons (H^+) from outside the membrane to inside. This process accumulates protons on the inside of the membrane, like water behind a dam, creating a concentration gradient. Potential energy is released and harvested by the ATP synthase complex. This protein cluster allows accumulated protons to rush to the outside of the membrane and transfers the energy released to ATP. ATP is the 'energy currency' or energy transfer molecule used throughout biological organisms.

PS I function

PS I is the second chlorophyll protein complex. It harvests energy from light by boosting an electron to acceptors. The elevated electron is replaced by the electron from PS II. The PS I electron energy is captured by various acceptors, all containing iron, and is finally used to produce NADPH. NADPH is used as a reducing agent in many biochemical reactions throughout the cell (Figure 43).
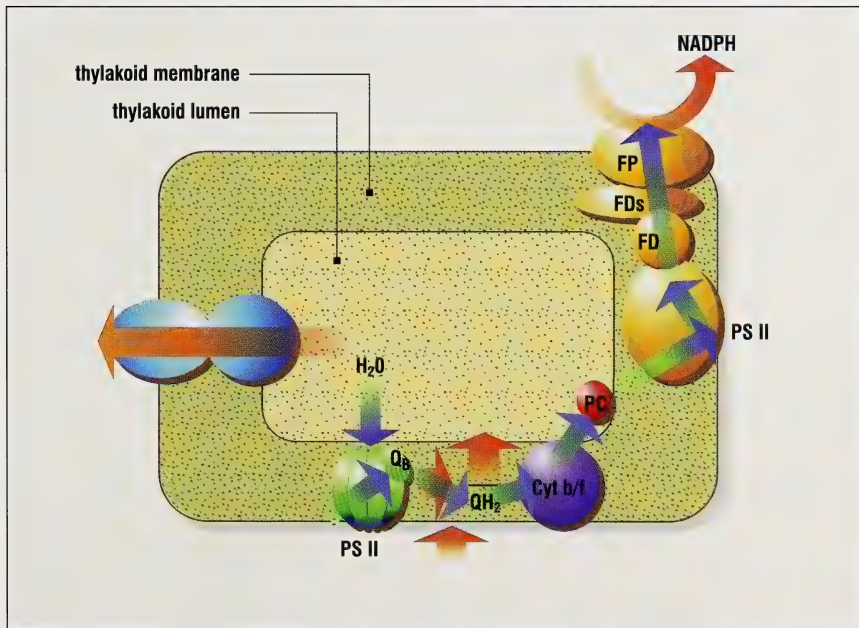
Figure 43. Pathway of electrons from PS II to PS I and NADPH. The blue arrows indicate the pathway of electrons from PS II to PS I. The red arrows show the flow of protons, first pulled into the lumen and then flowing outward into the stroma.

Inhibitors of PS II

- have a wide range of selectivity, allowing them to be used in many crops around the world
- may be subject to leaching into ground water
- vary widely in physio-chemical properties
- come from a variety of chemical families

Some of the oldest herbicides in use are inhibitors of PS II. They were developed in the 1950s and make up a large proportion of herbicides in use around the world. In North America, these herbicides play a small but important role. Some, such as bentazon and atrazine, are used primarily in corn and soy beans. Others, including bromoxynil and metribuzin, are used in small grain crops such as wheat.

Several herbicides affect the PS II target site. They have been organized into three different groups: Group 5, Group 6 and Group 7. Both chemical structure and physical chemical properties vary among these herbicides.

PS II inhibitors used in western Canada

	Class	Common name	Trade name(s)
Group 5	s-Triazine	atrazine	Atrazine, Laddok, Primextra Light, Shotgun*
	Uracil	bromacil	Calmix, Hyvar X/X-L, X-Over
		cyanazine	Bladex
		desmedipham	Betanex
	s-Triazinediones	hexazinone	Pronone 10G, Velpar
	Triazone	metribuzin	Crossfire*, Lexone, Sencor
		phenmedipham	Betamix*
	Pyridazinone	pyrazon	Pyramin
		simazine	Princep Nine-T, Simazine
Group 6	Benzothiadiazole	bentazon	Basagran, Laddok
	Nitrile	bromoxynil	Achieve Extra*, Buctril M*, Hoe Grass II*, Pardner, Platinum*, Thumper*, Unity*
		pyridate	Lentagran
Group 7	Substituted urea	diuron	Karmex, Krovar*
		linuron	Afolan F, Linuron 480, Lorox
	Amide	propanil	Stampede EDF
	Thiadiazole	tebuthiuron	Spike

* used in a mixture with another herbicide

Physical/chemical properties

This large, diverse group of chemicals has a range of chemical and physical properties. Some, like bromoxynil, are weak acids while others, like linuron, are not. Weak acid nature influences the rate of uptake into cells and phloem translocation.

PS II inhibitors are all moderately soluble in water. Water solubility increases the leachability of these herbicides in soil. The triazine herbicides, which are widely used at relatively high rates, have been found in ground water and thus are an environmental concern.

The soil adsorption properties of these herbicides is variable. Atrazine and cyanazine adsorption increases with soil acidity and soil organic matter. Thus, leaching increases in low organic matter soils, which are neutral or basic. Metribuzin is almost immobile in soils with high organic matter, but higher soil pH increases the mobility of metribuzin.

Some PS II inhibitors, such as atrazine, are subject to photo degradation on the soil surface. Most PS II inhibitors are not volatilized readily, either from soil or plant surfaces.

Inhibition of PS II electron transport

PS II inhibitors inhibit photosynthesis by binding to the Q_B binding protein in place of Q_B, the mobile electron carrier. Thus, they block the physical transfer of high energy electrons from PS II to the cytochrome b/f complex (Figure 44). Many weeds are resistant because the binding site has changed, prohibiting the binding of herbicides but not Q_B. While blocking photosynthesis reduces the amount of energy and, thus, the amount of carbohydrates formed, herbicide symptoms develop too rapidly to be accounted for by starvation.
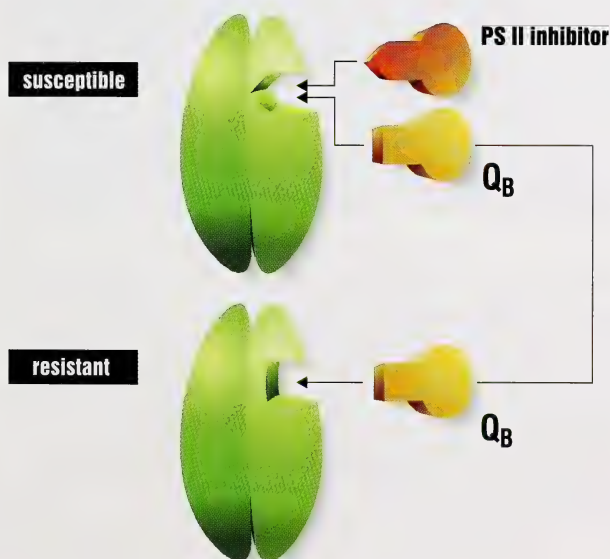
Figure 44. PS II inhibitors block the physical transfer of high energy electrons.

Herbicide symptoms and plant death are initiated by the blockage of high energy electron transfer. Light harvesting and the production of high energy electrons carries on even though Q_B is not transferring electrons to cytochrome b/f. These high energy electrons react with oxygen to form 'toxic radicals' that react with proteins and membranes making up the chloroplasts.

Because photosynthesis creates oxygen from water, oxygen is plentiful in chloroplasts. Some toxic oxygen radicals are always produced by normal photosynthesis. Plants have evolved a protective system that detoxifies toxic oxygen radicals. However, when a PS II inhibitor is used, this protective system is overwhelmed, and the toxic oxygen radicals attack the proteins and membranes. Proteins stop functioning and membranes become leaky (Figure 45). Photosynthesis ceases with the loss of membrane integrity and the cell stops functioning.
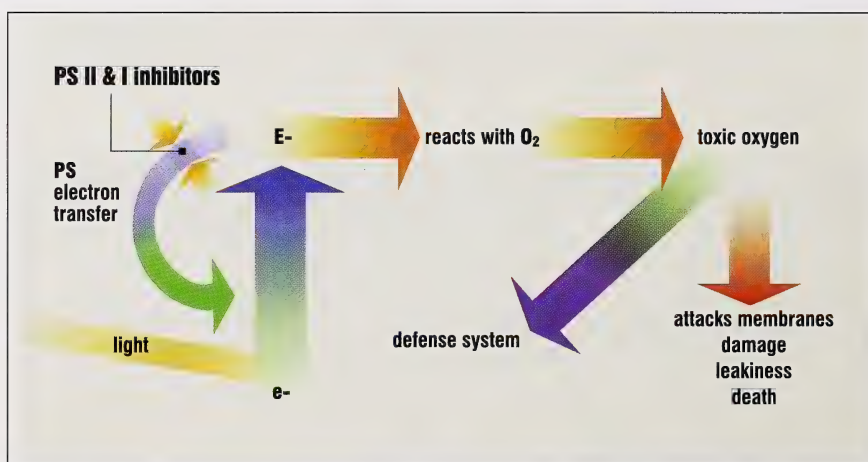
Figure 45. High energy electrons produced by PS II and PS I react with oxygen to produce toxic oxygen radicals. These radicals attack proteins and membranes in the chloroplast and cause damage. Damage is usually limited by the defense system, which neutralizes these toxic species. When PS II and PS I are blocked by a herbicide, toxic oxygen radicals increase and overwhelm the defense system.

Uptake and translocation

Weeds can take up PS II inhibitors through foliage and roots. Because most PS II inhibitors are sufficiently water soluble to move almost exclusively in the xylem, they have limited ability to move downward in the phloem. They tend to be swept in the xylem stream to the leaf edge, where symptoms become visible first. Water solubility also allows PS II to be taken up from the soil by roots.

Soil activity varies. Bentazon has almost no soil activity, while metribuzin can be absorbed through the roots to provide season long control of some weeds. Weeds that emerge through treated soil become chlorotic, turn brown and desiccate after two to five days in the sunlight, often before the weeds are noticed.

The rapid disruption of cell membrane reduces movement out of cells; thus, herbicides become trapped in a 'zone of death' and are not translocated in phloem.

Metabolism and selectivity

There are both selective and non-selective herbicides in this large group of products. Bromacil, diuron and tebuthiuron are non-selective and are used for roadside and industrial weed control only. All others are selective, in some crops.

Selectivity is based on differential rates and pathways of herbicide metabolism in the crops and weeds. Species selectivity is conferred by rapid herbicide metabolism to non-toxic metabolites by the crop but not by the weed.

A canola variety is under development that will rapidly degrade bromoxynil, making this canola tolerant, just as wheat is tolerant.

Symptoms

Symptoms include rapid chlorosis and necrosis beginning at leaf edges. Later symptoms include desiccation and a burned-off appearance of the leaves (Figure 46). Symptoms develop rapidly but require light for activity. Thus, symptoms develop most rapidly if full sunlight follows application.

Figure 46. The initial symptoms of Group 5, 6 and 7 herbicides include intra-veinal chlorois. Symptoms appear first at the edges of the leaves because these water soluble herbicides tend to get swept to leaf margins. Plants eventually desiccate.

Toxicity

The toxicity of these herbicides varies considerably.

The large values in the table below indicate that more herbicide was required to kill one half of the test population of rats. Thus, herbicides with larger LD_{50}s are less toxic.

Comparative acute oral toxicity of PS II inhibitors

Common name	Trade name(s)	LD$_{50}$ (male rats mg/kg)
atrazine	Atrazine	3090
cyanazine	Bladex, Blagal	182 - 334
metribuzin	Crossfire*, Lexone, Sencor	1090
hexazinone	Pronone 10G	1690
bromoxynil	Achieve Extra*, Buctril M*, Hoe Grass II*, Laser*, Pardner, Thumper	440
bentazon	Basagran	1100
bromacil	Hyvar X/X-L	5175
linuron	Afolan F/Linuron 480/Lorox	1254
diuron	Karmex	3400
tebuthiuron	Spike	644

* used in a mixture with another herbicide

Implications for application

- Some PS II inhibitors may leach in soils with low organic matter. Potential for movement in soil water is increased by irrigation and rainfall.
- These herbicides work better on small, emerging weeds than on large weeds.
- When formulated as wettable powders, these products can be hard on equipment.
  - use vigorous agitation
  - do not leave in tank and lines overnight as plugging may occur
  - flush system thoroughly after use and clean screens and filters
- Rapid activity of PS II inhibitors limits their usefulness on perennial weeds.
- Adequate coverage with relatively high volumes of water increases weed control and crop tolerance.

Inhibitors of PS I

- non-selective herbicides
- affect photosynthesis at the PS I site
- cause rapid desiccation
- act primarily as contact herbicides
- bind irreversibly to clay soils
- have only foliar activity

PS I inhibitors are fast acting, non-selective, contact herbicides. Paraquat is generally more active on grasses, while diquat has increased activity on broad-leaved plants.

	Class	Common name	Trade name(s)
Group 22	Bipyridilium	paraquat	Gramoxone, Gramoxone PDQ
		diquat	Gramoxone PDQ, Reglone, Reglone A, Reglone Pro

Physical/chemical properties

Both paraquat and diquat are highly water soluble and are not weak acids. Both are positively charged and bind extremely tightly to soil, primarily to clay particles but also to organic matter. Once bound, the inhibitors are unavailable to both plants and soil microbes. Thus, they do not have soil activity and do not leach.

Paraquat and diquat can be photo degraded to some extent on leaf surfaces, but the loss is too slow to affect activity.

Uptake and translocation

Paraquat and diquat are rapidly taken up into the leaf. They are rainfast in one to two hours. Tight binding to soil means they are not available to be taken up by plant roots. Movement is almost exclusively in the xylem, from base to top of the plant; however, rapid activity limits movement.

Inhibition of PS I electron transport

Unlike PS II inhibitors, PS I inhibitors do not block electron flow but rather divert electrons from the iron-containing electron carriers FP, FDs and FD (Figure 42 and 43). Diverted electrons are passed to oxygen, thus forming toxic oxygen radicals and finally, the ultra reactive hydroxyl radical (Figure 45). The herbicide is not destroyed in the process. Instead, it acts as a catalyst, regenerating after passing on the electron, so it may receive another electron from PS I.

Radicals disrupt protein and lipids. Plant membranes are attacked and become leaky, resulting in tissue desiccation and plant death. The rapid activity of these inhibitors permits them to be used as crop desiccants as well as herbicides.

The rapid activity of these herbicides also hinders their movement in the phloem. Because they can only translocate from living cells, these herbicides can become trapped in the zone of death they create.

Metabolism and selectivity

Neither paraquat nor diquat are metabolized by plants and both are non-selective. There are differences in susceptibility between these two herbicides; however, the reasons for the differences are not well understood.

Toxicity

These herbicides are highly toxic to mammals, including humans (LD_{50} = 120 - 230). Exposure to eyes, lungs and respiratory tract (inhalation) causes irritation if precautions are not taken. Protect yourself by reducing exposure to these herbicides.

Symptoms

Wilting and inter-veinal chlorosis (yellowing) appear within hours of application if plants are in the light. This stage is followed by browning and blackening of the leaf edges and complete browning and desiccation of the leaves (Figure 47).

Figure 47. Initial symptoms of Group 22 herbicides include spotting and chlorosis. These herbicides cause extremely rapid desiccation.

Implications for application

- These rapid-acting herbicides can be more effective if sprayed in the evening as they have an opportunity to move into the plant before herbicide action limits their movement.
- Good coverage is essential for activity. Higher water volumes are more effective.
- More effective on small weeds. Increase water volume if spraying larger weeds.
- Diquat is preferred to paraquat for desiccation.
- Rainfast within one to two hours.
- When used as a crop desiccant, rapid activity can increase pod shattering in some crops.
- Inactivated by muddy water.

Herbicide Resistance

- herbicide resistance poses a challenge to conventional agriculture
- many weeds have been selected for resistance in Western Canada
- resistance can be conferred by different mechanisms
- resistance may be prevented or delayed
- early identification of herbicide resistant weeds is critical
- focus in the future is on herbicide resistance management

Herbicide Resistance – A Challenge to Conventional Agriculture

The selection of herbicide resistant weeds poses a challenge to conventional agricultural practice. Fortunately, it is a concern that may be avoided or delayed by careful management.

In the late 1940's, farmers began to use the herbicide 2,4-D, a new tool to combat weed problems. This was the first selective herbicide used in crops. Applied post-emergent, 2,4-D allowed producers to control broad-leaved weeds in cereal crops. For the first time, producers were able to achieve adequate control of some weeds, without either injury to crops or tillage.

Since 2,4-D, many herbicides have rapidly been adopted by producers. Herbicides have continued to improve, providing more targeted weed control, improved crop safety and activity at very low rates (as low as 4 g/acre or 10 g/ha). The introduction of herbicide tolerant crops, in which non-selective or broad-spectrum herbicides can be applied, has enabled producers to achieve excellent weed control in non-competitive crops.

Modern cropping systems have evolved that are more sustainable, productive and economically viable than in earlier years. However, these systems depend on herbicides for weed control. Therefore, the occurrence of herbicide resistant weeds threatens current cropping practices. Herbicide resistant weeds present a new challenge to producers.

What is herbicide resistance?

Three conditions must be met before a weed is **herbicide resistant:**

1. It must normally be controlled by the herbicide.
2. It must survive a usually lethal rate.
3. The change must be heritable, that is, seeds produced from the resistant plant must also be resistant.

Resistance can be quantified by comparing experimental values derived from resistant and susceptible biotypes. The rates that control 50 per cent of the weed population (LD_{50}), that cause a 50 per cent reduction in plant biomass or that reduce enzyme activity by 50 per cent (I_{50}) are compared. An example of a typical comparison of resistant and susceptible weed biotypes is shown in Figure 48. It also shows that resistance levels can vary: one biotype is highly resistant and one moderately resistant.
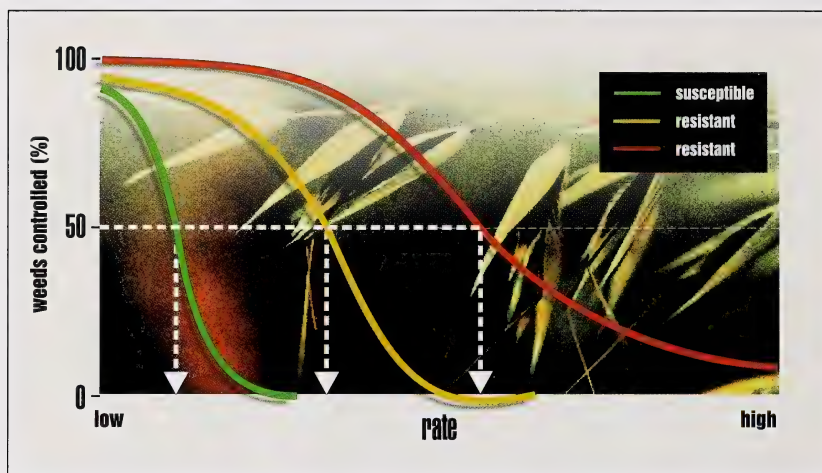
Figure 48. Response of susceptible and resistant weeds to a herbicide applied at increasing rates. More herbicide is needed to control the resistant population.

Weeds usually become resistant to some or all herbicides in the same group (Chapter 1, table on pages 2 and 3). Resistance within herbicide groups is frequently called **cross-resistance**. Some weeds become resistant to herbicides from *more* than one group and are called **multiple herbicide resistant**. These multiple herbicide resistant weeds are the most difficult for producers to control.

Two other terms are frequently used when herbicide resistance is discussed: **tolerance** and **susceptibility**. Many plants are naturally **tolerant** of certain herbicides. Crop plants are tolerant of selective herbicides, and weeds are tolerant to some herbicides. For example, cleavers is tolerant of the herbicide Muster while wild mustard is controlled. Similarly, green foxtail is tolerant of Assert while wild oats is controlled. However, wild mustard is **susceptible** to Muster, and wild oats is **susceptible** to Assert at the recommended rate under good growing conditions.

Relative susceptibility and tolerance of a weed and crop are usually rate dependent. These factors also depend on both the growing conditions of the weed/crop and the stage of development, and they may differ slightly from weed population to weed population or among crop varieties. Herbicide rate and growth stage recommendations on herbicide labels are designed to consider these variations in relative susceptibility and tolerance.

Resistant Weeds in Western Canada

Western Canada has several resistant weeds reported (Figure 49). However, the incidence of herbicide resistant weeds varies among the provinces. Manitoba has reported more multiple herbicide resistant wild oats than Saskatchewan and Alberta, while Alberta has the largest occurrence of Group 2 resistant chickweed. The distribution of resistant weeds may be related to herbicide use patterns and the abundance of weed populations. For example, Manitoba uses Group 1 products intensely, leading to more Group 1 resistant wild oats. Chickweed is very common in central Alberta, contributing to a Group 2 resistant chickweed.

Wild mustard

Chickweed

Russian thistle

Green foxtail

Kochia

Wild oats

Figure 49. Western Canada has a number of weed varieties resistant to herbicides

Cleavers

Spiny annual sow-thistle

Herbicides in some groups have either not selected or have selected very slowly for resistant weeds. 2,4-D, MCPA and other Group 4 herbicides have been used extensively for many years with few problems. These should be considered lower risk herbicides than Group 2 herbicides, which selected resistant weeds within five years of their introduction. In Western Canada, no weeds are resistant to Group 9 (Roundup) or Group 10 (Liberty) herbicides at present.

Herbicide resistance has become a problem for producers in the last 10 years. Resistance was first reported with Group 8 herbicides (Avadex and Avenge). This was followed quickly by broad-leaved weeds resistant to Group 2 herbicides (Ally, Refine Extra and Pursuit), green foxtail resistant to Group 3 herbicides (Treflan and Edge) and wild oats resistant to Group 1 herbicides (Puma, Achieve).

Weeds Resistant to Herbicides in Western Canada

Group	Herbicide(s)	Weed	Number of Sites
1	Some or all of the Group 1 herbicides	green foxtail, wild oats	>200
2	Muster	wild mustard	1
2	Some or all of the Group 2 herbicides	chickweed, cleavers, hempnettle, kochia, russian thistle, spiny annual sow-thistle, wild oats	>200
3	Edge, Treflan	green foxtail	>200
4	2,4-D and other Group 4 herbicides	wild mustard	1
5	Sencor	wild mustard	1
8	Avadex, Avenge	wild oats	>200
16	Nortron	wild oats	<5
1, 2, 8, 25	Assert, Avadex/Avenge, Mataven, Puma	wild oats	<20
2, 4	Accord and Group 2 herbicides	cleavers	1

The total number of fields with resistant weeds and the number of acres infested are difficult to estimate. Some cases of resistance have not been reported, either because testing was done by many different individuals or agencies or because some producers recognized the problem independently and have not had weeds tested.

Severity of the resistance problem

The difficulties a producer has following the development of a herbicide resistant weed population varies with the **weed** and the **availability of alternative control products**.

In many fields in central Alberta, Group 2 resistant chickweed is present; however, Group 2 herbicides are still used routinely. In this instance, chickweed is a part of a large group of weeds that infest the fields, most of which are controlled very well by a Group 2 herbicide. Chickweed control is maintained by the addition of another herbicide from another group, frequently applied with a Group 2 product in a tank mix. Weed control is more expensive and requires more consideration, but farming practices are not significantly different due to the presence of herbicide resistant chickweed.

Wild oats resistant to Group 1 herbicides and multiple resistant wild oats are a much more serious problem. Wild oats are a serious weed that can severely limit yields in all crops. Group 1 resistance excludes the most effective wild oat herbicides, and products that provide effective control are limited. Multiple herbicide resistant wild oats, where control is limited to fewer selective herbicides, can mean dramatic changes in cropping practices and weed management.

Herbicide Resistance Development

"Herbicide resistance is a numbers game." *Steven Powles, Australian Weed Scientist.*

Selection for herbicide resistance

Weed populations are genetically diverse; they are composed of individuals with a range of characteristics. And like all organisms, weeds adapt to changes in their environment. Weed management practices, like tillage and herbicide application, exert a tremendous pressure on weed populations to adapt. It is this genetic diversity that allows weeds to adapt to the many different management practices.

When a herbicide is applied, it puts a selective pressure on weed populations. Most of the plants are killed and contribute no seeds to the weed seed bank. However, if a plant is not controlled by the herbicide because it is resistant, it will likely produce seed. This new seed will cause an increase in the seed bank of plants not susceptible to the herbicide. If the selection pressure is maintained (herbicide from the same group used again and again), the rate of seed bank increase is dramatic. If selection pressure is varied, the rate of increase is slow.

Resistant plants exist in very low numbers in the population, from 1 in every 10^6 to 1 in 10^{30}; however, there are many individual weeds in the average field. For example, if there are 100 green foxtail in each square metre, there are 64 million weeds in each quarter section. If the resistant gene is present at 1 in 10^6 (1 in a million), there are 64 resistant plants in the field before selection. Weeds that first developed herbicide resistance are abundant, like wild oats, green foxtail and chickweed.

Because resistant weeds are present in such low numbers in the field initially, it takes a long time for them to increase sufficiently to be noticed by the producer. Resistant weeds usually make up from 10 to 30 per cent of the weeds in a field before producers notice them.

Some weeds, like wild oats, are primarily self-fertilizing while others, like wild radish, must cross-fertilize with another individual. Weeds that out-cross have a higher chance of exchanging genetic resources, making new combinations available to offspring. Evidence from other countries indicates that out-crossing weeds are most likely to accumulate multiple herbicide resistance mechanisms. This may explain why wild oats have developed multiple herbicide resistance relatively slowly, compared to rye grass in Australia or black grass in Europe.

Mechanisms for surviving herbicides

Scientists have identified several mechanisms that result in weeds becoming resistant to herbicides. While not all these mechanisms have been identified in Western Canada, they illustrate that weeds can adapt to survive herbicides and may well appear in the future.

Target site resistance

All herbicides bind to and interfere with a specific site in plants. Most of the herbicide target sites have been identified, and these sites form the basis for grouping of herbicides (See Chapter 1, table on pages 2 to 4). Herbicide target sites are proteins, usually enzymes, but they can also be proteins that transfer electrons or contribute to hormone regulation in plants. Because proteins are encoded by DNA, mutations may cause small alterations in proteins that are heritable, passed along from mother plant to seed.

If the target protein is altered so that a herbicide does not affect the enzyme and yet the protein still functions, the plant may be resistant to that herbicide (Figure 50). Target site changes frequently confer resistance to high rates of herbicides and often confer resistance to some or all herbicides that interfere with the same target site (i.e., herbicides in the same group).
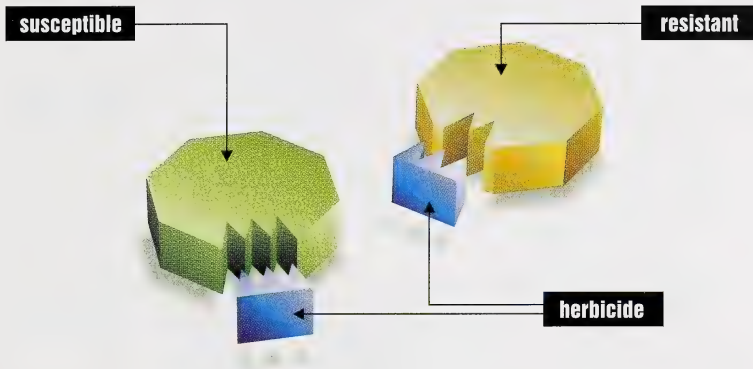
Figure 50. Weeds may be resistant due to a change in the target site that prevents the herbicide from blocking enzyme activity.

Target site resistance has been the type of resistance most common in Western Canada. For example, chickweed selected for herbicide resistance to Glean results from a change at the target site. In some cases, only a small difference in the enzyme can confer high levels of resistance. For example, the change of a single amino acid in the ALS enzyme, the target site of the Group 2 herbicides, can confer high levels of resistance to most Group 2 herbicides.

Herbicide rotations have been recommended as a method to delay or prevent herbicide resistance. Figure 51 shows the selection of herbicide resistant weeds in three situations: under continuous herbicide use, with rotation every one in two years and with a rotation of one in three years. The number of applications of herbicides from the same group is the most critical factor in the rate of selection for herbicide resistance.
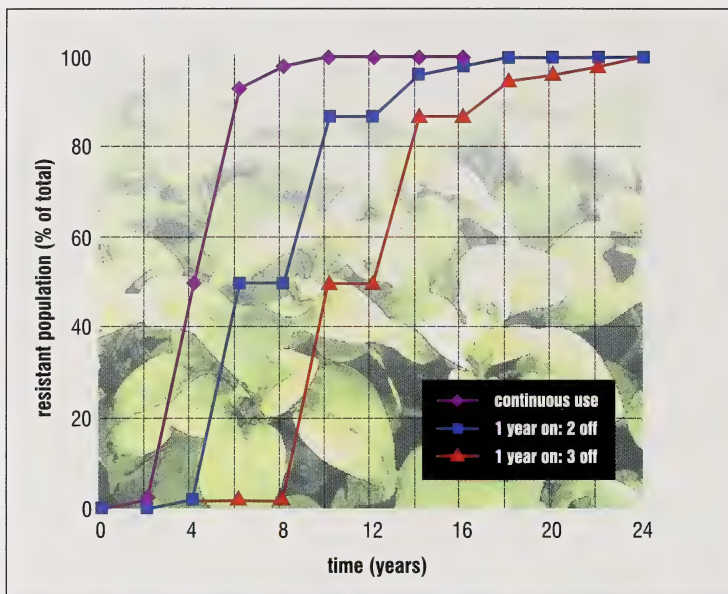
Figure 51. Increase in herbicide resistant weeds when herbicides are used continuously or rotated.

Varying the herbicides used in a field (by herbicide group) reduces selection pressure and delays the selection of herbicide resistant weeds. Note that the proportion of herbicide resistance in the population does not decrease when the herbicides are rotated. The proportion remains the same until the herbicide group is used again.

Selection for target site resistance can be decreased by the use of low-residual herbicides. If residual and non-residual herbicides have the same site of action and similar control, residual herbicides select a larger number of weeds than non-residual. Target site resistance can be selected by both high and low herbicide rates. Selection is faster at higher rates because fewer susceptible weeds escape to produce seed.

Herbicide metabolism

Herbicide metabolism is the second most common mechanism of herbicide resistance worldwide. This mechanism means that many selective herbicides are detoxified (metabolized) rapidly by crop plants, but not by weeds. However, weeds can be selected for the ability to degrade herbicides rapidly (Figure 52).
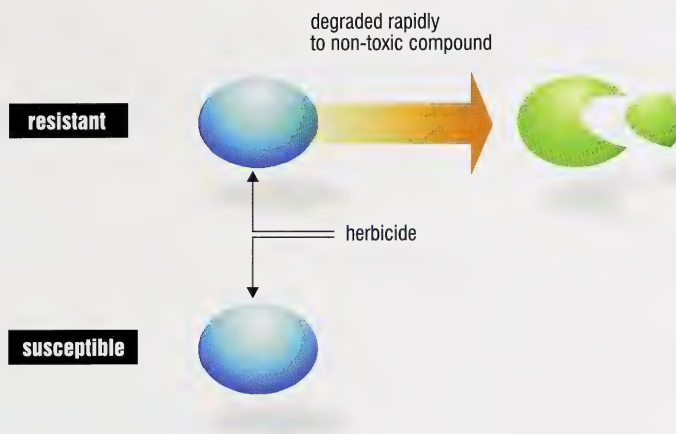
Figure 52. Some resistant weeds can rapidly degrade the herbicide to a non-toxic compound while the susceptible weeds cannot. In susceptible weeds, the herbicide remains in the toxic form.

Metabolism-based resistance can confer resistance to lower rates of herbicides than target site resistance, but it may confer resistance across herbicide groups (multiple herbicide resistance). In Western Canada, this mechanism confers resistance in wild mustard to the herbicide Muster; however, these weeds are still controlled by other Group 2 herbicides.

Rapid growth

Recent research suggests that wild oat resistance to Avadex and Avenge may not involve either the target sites of these herbicides or enhanced herbicide metabolism. Wild oats that have become resistant tend to have high germination (low dormancy) and emerge rapidly from the soil. Evidence suggests that resistant wild oats may have higher levels of the plant hormone gibberellic acid. These high levels may allow the plants to simply 'outgrow' the effects of Avadex and Avenge. Work is in progress to clearly define this mechanism of resistance.

Other mechanisms

Weeds are remarkably adaptable. Over 100 herbicide resistant weed species have been reported, along with many resistance mechanisms. While not all the mechanisms that weeds will develop can be predicted, weeds will certainly continue to be selected under current intensive herbicide use.

Multiple herbicide resistance

In a small number of situations, weeds have become resistant to herbicides in more than one group. This result can occur in two ways:

1. The weeds can have a mechanism that confers resistance to herbicides from more than one class.
2. The weeds can have more than one mechanism.

An example of the first situation would be a weed that has been selected to degrade or metabolize both Puma (Group 1) and Assert (Group 2). No evidence exists as yet from Western Canada, but weeds from England and Australia are known to have this mechanism.

Weeds containing different herbicide resistance mechanisms can cross-pollinate so that the seeds produced have two herbicide resistance mechanisms. While there are no documented cases in Western Canada, weeds from England and Australia are known to have multiple herbicide resistance mechanisms.

Identification of Herbicide Resistant Weeds

Diagnosing herbicide resistance in the field

Many factors other than resistance cause poor or intermittent weed control in the field. The weed stage of development affects herbicide control. In general, a weed is easier to control when it is younger. When a herbicide is applied to older weeds, control can be ineffective. Diagnosing the cause of poor weed control is complicated by the presence of multiple weed flushes.

Growing conditions of the weed before and after spraying also affect weed control. In general, weeds are easiest to control when they are growing rapidly. Drought, heat and cold reduce weed growth and also decrease weed control. Pre-emergent herbicide control is complicated by incorporation, herbicide volatilization and differences in soil conditions (organic matter, moisture, temperature), which can vary across the field.

Application error – including spray misses, incorrect sprayer calibration or improper mixing of herbicides and surfactants – and even the time of day of application affect herbicide control. Careful consideration is necessary to determine the following: if the correct rate of herbicide was applied, at the right time, with the correct surfactant, on weeds at the correct stage and under good growing conditions. When all other factors and possible influences have been eliminated, herbicide resistance should be suspected.

Patches

Herbicide resistant weeds are frequently seen in patches in the field. When the patch shape is irregular, it is unlikely to be associated with the spray pattern. Instead, the irregular patch shape reflects the seed spread from the mother plants. Patches generally occur early in the development of resistance, before weeds have spread throughout the field.

Field tests

If resistance is noticed early after spraying, it is frequently possible to re-apply the herbicide to a small weed patch to check if the weeds can be controlled. However, it is difficult to achieve a correct field rate with a hand-held sprayer. There is usually a tendency to over-apply, possibly giving a false negative result. Resistance to lower rates of the herbicide could exist, but the over-application could mask this problem by having the weeds die due to the high rate of application.

Testing facilities on the prairies

If resistance is suspected, seeds should be collected and sent away for testing. Both careful collection of viable seeds and good seed handling are required for successful testing. Testing should include both the products that failed in the field and potential alternative herbicides. Because herbicide resistance is variable, herbicides that could be used on the weed should be tested, including herbicides from the same group. In some instances, for example, the herbicide Select can still be used on weeds resistant to other Group 1 herbicides. Producers need to know which herbicides will work and those that will not.

Testing for herbicide resistant weeds can be done at the following locations:

Crop Protection Lab
3211 Albert Street
Regina, Saskatchewan S4S 5W6
Telephone: (306) 787-8130

Ag-Quest
Box 144
Minto, Manitoba R0K 1M0
Telephone: (204) 776-2087

Prevention or Delay

Herbicide resistance is a new phenomenon, and many aspects of resistance are just beginning to be understood.

Vary weed control measures

Herbicides are only one tool of many that can be used to manage weed populations. For example, judicious tillage continues to play an important role, especially where weed populations are high. Crop rotation that includes highly competitive crops (such as barley and forages) will reduce the reliance on herbicides.

Pre-seeding tillage or pre-seeding non-selective herbicide application can reduce weeds that need to be treated in-crop. Agronomic practices that optimize the competitive ability of the crop will reduce weed pressure and will allow herbicides to work more effectively. These practices include increased seeding rates, optimum levels of fertilizer banded with or near the seed and narrower row spacing.

Determine weeds at risk

Weeds at risk are those that are the most numerous and that have already developed herbicide resistance (see table on Weeds Resistant to Herbicides in Western Canada).

Determine herbicides at risk

Herbicides at risk are those that have been used extensively and those from high risk groups. For example, many fields have a long history of Group 1 use. These fields should be considered at risk, and alternative herbicides should be used from different herbicide groups.

Herbicides are not all the same from a resistance perspective. Some herbicides select for resistant weeds more quickly than others. Herbicide risk is calculated by the number of applications that have been required previously (here or in other parts of the world) to select for herbicide resistant weeds. After a number of applications have been used on a field, the risk of having herbicide resistant weeds in large numbers in that field increases dramatically (Figure 53). Not enough information is available for all herbicides, so herbicides not listed must be considered unknown.
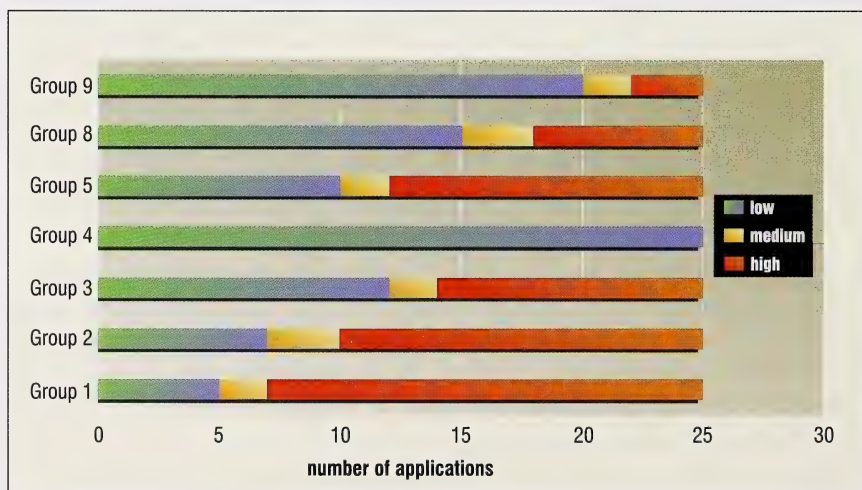
Figure 53. Estimations of the relative risk of selection for resistant weeds by herbicide from some herbicide groups.

A risk assessment should consider:

- What weeds are present?
- Are the weeds numerous?
- How many applications of a single herbicide group have been made to the field?
- Is the herbicide in a low, medium or high risk category?

Vary herbicide used by group

To delay the selection of herbicide resistant weeds, producers should rotate the herbicide groups on a field-by-field basis. However, realize that rotation does not prevent resistance. The grower does not change the proportion of resistant and susceptible weeds in the field by rotation away from a herbicide group. Resistance does not disappear. Whenever the group is used again, the selection increases again (See Figure 51, Increase in herbicide resistance).

Reduce weeds selected

Producers can extend the use of high risk herbicides by not using them when weed numbers are high. The more weeds treated, the more likely a resistant weed will be present and selected. In fields with high weed numbers, tillage or the use of a low risk herbicide may be a better option.

Include herbicide mixtures

Herbicide mixtures or sequential applications can be useful in delaying resistance if the following conditions apply:

- both herbicides affect the same weed and
- the partners come from different herbicide groups

Good mix partners must have similar residual properties. Crossfire is an example of an effective herbicide mixture. It contains tribenuron (Group 2) and metribuzin (Group 5). Both components control chickweed, hempnettle, lamb's quarters and wild mustard with similar residual effects, so they are an effective way to delay the selection of Group 2 resistance.

Avoid residual herbicides

Highly residual herbicides apply a continuing selection pressure on a weed population, effectively selecting more individuals than a short residual herbicide. Where possible, a short residual herbicide is preferable. For example, Odyssey or Harmony Gold may be a better choice than Pursuit in Smart canola, because of differences in residual length.

Use certified seed and clean management practices

Using certified seed can reduce the input of weed seeds into the field. This simple step can slow the onset of herbicide resistance.

Monitor for suspicious weed patches

The sooner resistant weeds are noticed, the more control options remain open. By monitoring fields for suspicious weed patches, producers can avoid severe problems.

Management Strategies

The most significant aspect to consider is that herbicide resistance will not go away, even if the problem herbicide is no longer used.

Seed-bank management

When herbicide resistance develops, the weed population is changed permanently. The management of resistant weeds must concentrate on reducing the number of weed seeds in the seed bank. Do not allow weeds (especially resistant weeds) to go to seed.

Site-by-site

The control of herbicide resistant weeds must be achieved on a site-by-site basis, depending on the weed and the herbicides it is resistant to. Resistance and cross-resistance vary considerably. Test all potential herbicides to determine which ones work and which ones do not.

Patch control

Resistant weeds are normally noticed while still in patches in the field. Patches that cannot be explained by a herbicide miss should be controlled immediately. Spray the weeds with a non-selective herbicide like Roundup or Touchdown. Take the weed and crop off as silage or hay or till the weed patch. Do not let weeds go to seed.

Non-selective herbicide options

Examine your herbicide options. If possible, consider delaying seeding and controlling initial weed flushes with pre-seeding Roundup/Touchdown or other non-selective herbicide.

Consider planting a herbicide tolerant canola to allow the use of Roundup or Liberty for non-selective weed control. These products help reduce the number of weed seeds in the seed bank and are considered relatively low risk.

Other weed control options

Plant competitive crops, like barley and wheat, using a high seeding rate, so weeds are suppressed by the crop. Consider planting forages in fields that contain herbicide resistant weeds because perennial crops are highly competitive with weeds. Rather than using a herbicide, consider silaging to stop weed seed set if weeds become a problem.

Low vs high rates?
Considerable debate exists as to whether or not low rates hasten the selection of herbicide resistant weeds. Many producers have found they can achieve adequate weed control with herbicide rates lower than those recommended under good growing conditions. As long as herbicide control is adequate, there should be no major difference in the selection pressure.

Stop spread of resistant weeds

Do not move herbicide resistant weed seeds to other fields with farm equipment. Cover grain loads with a tarpaulin to stop weed seed dispersal.

Looking Ahead

Herbicides will continue to be the primary means to control weeds in the foreseeable future. New herbicides are becoming available every year and will make a contribution to the control of herbicide resistant weeds; however, these herbicides will also select for resistance. It now takes 10 years to bring a herbicide through the development stages and then to market. Unfortunately, weeds can be selected for resistance in less time than that.

Herbicide tolerant crops will continue to be developed and will play an important role in an integrated weed management strategy. However, volunteer herbicide tolerant crops will add a new dimension to herbicide rotations and may become weeds in themselves.

In the future, multiple herbicide resistant weeds will continue to be selected and will continue to make weed control more costly and difficult. Because more weeds will be selected for herbicide resistance, prevention and control are key strategies to focus on.

Dose Transfer

- during transit from the nozzle to the site of action, a herbicide spray encounters many obstacles that reduce the available dose
- a hydraulic nozzle generates a broad droplet size spectrum, which ensures that some portion of the spray always reaches the target
- small droplets drift and evaporate rapidly, but are more easily retained by some targets
- large droplets penetrate some canopies better, but are more likely to bounce off plant foliage
- uniformity of deposition is more important than choosing any single optimum droplet size
- getting the most active ingredient to the target involves a knowledge-based compromise of many counteracting factors that are often weed, herbicide, and active ingredient specific

Dose transfer refers to the processes involved in getting the active ingredient from the sprayer to the target. The processes are complex and many effects are counteracting (Figure 54). For example, using coarse sprays decreases drift, but their use may also decrease spray retention on some species of plants. Inevitably, compromises are made; therefore, when modifying the process, keep the entire process in mind rather than focusing on a single goal.
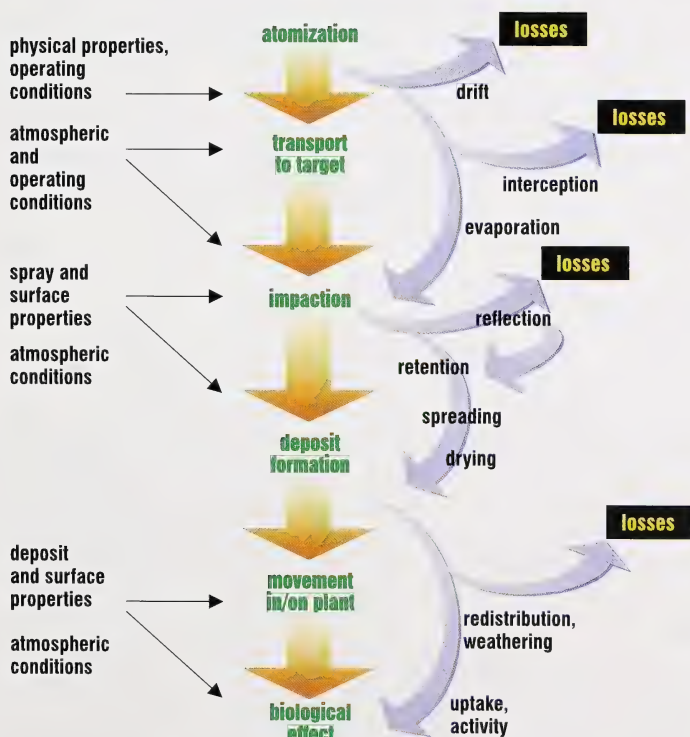
Figure 54. Processes and factors influencing dose transfer from the sprayer nozzle to the target. **Source 1**

79

Overview

Atomization

The way crop protection agents (CPAs) are atomized has changed little in the last 100 years. The primary nozzle used around the world is still the hydraulic flat fan, which, in its most basic form, is relatively unsophisticated. **Hydraulic nozzles** use pressure as the energy source to atomize the spray liquid. These nozzles produce sprays that contain a wide variety of droplet sizes. This property has often been criticized as being wasteful, as smaller droplets drift and evaporate readily, and larger droplets provide poor coverage and may bounce off the target. Yet these sprays remain popular because they provide consistent results over a variety of conditions.

The droplet size resulting from atomization is governed by the nozzle type, flow rate, spray pressure, travel speed and the physico-chemical properties of the spray liquid.

Transport to target

Once the spray is atomized, it must reach its intended target. In many ways, this stage is the most important and most difficult-to-control part of dose transfer. Having left the nozzle, the spray is now subject to the environment. Droplets immediately begin to evaporate. The smaller droplets slow down considerably. Under dry and/or windy conditions, drift may occur. Along the spray's path to its target, an interfering crop canopy can present barriers to penetration. Significant losses can occur before the spray encounters the target.

The applicator has some control over these losses. The type of nozzle and the properties of the spray solution can affect the transport of the spray. Coarser sprays will be less likely to drift, and the use of air assist or a reduction in travel speeds can enhance canopy penetration. Oil-based formulations can reduce evaporative losses. But these choices may affect the next stage of dose transfer.

Impaction and retention

After reaching the crop canopy, the spray must make contact with the target. The likelihood of contacting the target depends to a large degree on two factors: the **capture efficiency** of the spray by the target (a measure of a target's ability to intercept incoming droplets) and on **spray and leaf surface properties**. Compromises now must be made, because the droplets most likely to avoid drift and penetrate the canopy may also be more likely to bounce off leaves. Smaller droplets will be more easily retained by vertically-oriented surfaces like grasses. No one droplet size can meet all the goals of the application.

Deposit formation

The form of the spray deposit can profoundly affect the efficiency of the herbicide. Once a drop is retained, it begins to form a deposit. The droplet spreads and dries and then presents the active ingredient to the pest or plant material underneath. These processes are again controlled by carrier volume, droplet size and formulation, and the

importance of effects will depend on the active ingredient and target plant. For example, spray coverage is more important for a contact herbicide than for a systemic one. An adjuvant may provide more spread (coverage), but it may also increase the rate of evaporation, providing less opportunity for uptake. Once again, a number of variables will need to be optimized simultaneously.

Movement in/on plant

Some of the most important barriers still exist once the spray is deposited on the target surface. Before drying, the deposit may redistribute to another region of the plant, where efficacy may be changed. Spray deposits can weather before they are absorbed through photodegradation or by rainfall washoff. The degree of contact established between the droplet and the leaf surface will be a function of the leaf surface characteristics and the spray liquid properties. Herbicide uptake and translocation (see Chapter 1) are also governed by formulation and droplet size. The addition of the correct adjuvant is often required for the uptake of foliar herbicides. Droplet size may affect uptake: size controls coverage of the target, as well as whether localized damage (the result of too large a droplet concentrating too much active ingredient or surfactant in a small area) will occur.

Biological effect

The elusive biological effect is the net result of all the factors governing the dose transfer. It requires significant compromise to achieve the best results. The application of a very fine spray to obtain gains in spray retention may well be offset by increases in drift and evaporation. Too coarse a spray will reduce drift, but may result in less spray retained. One reason why the hydraulic nozzle has survived for so long is because it successfully balances the many variables most of the time. It produces both fine and coarse sprays, both fast and slow moving droplets.

Why is this important?

The use of crop protection agents (CPAs) is under increasing scrutiny in our society. Pesticides have a bad public image, so it is ever more important to demonstrate responsible use and good stewardship of this technology. The foremost goal should be to apply the correct rate of a registered product to the target area using approved means. This statement means doing everything possible to prevent operator exposure, spray drift or other means of off-target transport. If this task cannot be accomplished, more stringent steps may be taken by governments to ensure that these chemicals are used properly.

Other countries have already experienced government intervention in the use of CPAs. Programs have been enacted that mandate the reduced use of CPAs, and residue limits of CPAs in the environment have become stricter. Only responsible use can prevent the same thing from happening in Canada.

The importance of the applicator
There is no one application method, no one foolproof technology that will ensure that products will be applied properly. This task remains the responsibility of the applicator.

Atomization

Basic processes

When spray liquid is forced, under pressure, through the elliptical orifice of a flat fan nozzle, a flat sheet of liquid results. This sheet quickly encounters resistance from the surrounding air and becomes unstable. Holes begin forming in the sheet, and ligaments of spray liquid begin to break free. Soon, these ligaments break into smaller pieces that go on to form the droplets of the spray (Figure 55). The entire process takes as little as a few milliseconds, and the average spray sheet extends only about one cm from the nozzle tip. But the spray sheet is pivotal in determining the kind of spray pattern and droplet size spectrum that results.
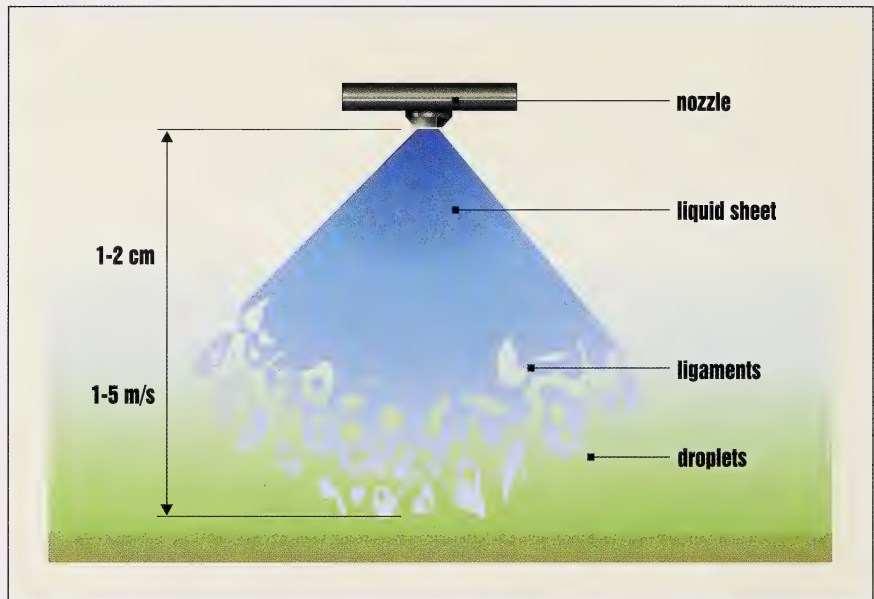
Figure 55. Sheet breakup in a flat fan nozzle – from a solid liquid sheet – becoming unstable, forming ligaments and finally breaking into droplets.

The spray coming off the liquid sheet is comprised of droplets of various sizes; for a typical flat fan nozzle (XR8003), droplets range anywhere from 5 μm to 700 μm in diameter. In a typical spray, the vast majority of the droplets are very small – usually, about 80 per cent of the total number of droplets in a spray are less than 100 μm in diameter (Figure 56).
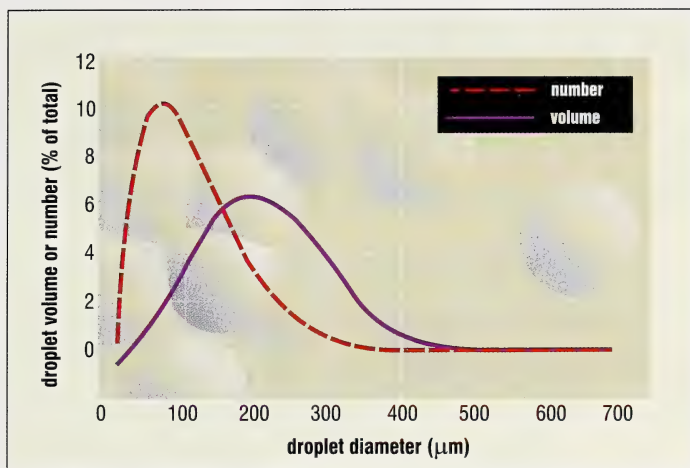
Figure 56. Typical droplet size spectrum emitted by a flat fan nozzle, by number and by volume.

Since the volume of a droplet has a cubic relationship with droplet diameter, the volume distribution looks completely different from the number distribution. The majority of the spray volume is in droplets between 300 and 500 μm. Small droplets (< 100 μm) make up only about 10 per cent of the total spray volume. The makeup of the spray in terms of droplet size and velocity is called the **droplet size (or velocity) spectrum**.

Droplets are emitted from the nozzle at a very high speed, approximately 20 m/s (70 km/h), but begin to slow down immediately. By the time the spray reaches its target, about 50 cm below the nozzle, speeds are much reduced (Figure 57).
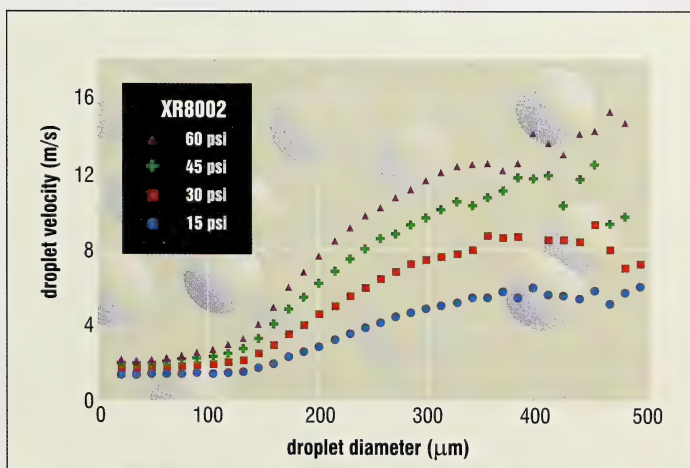
Figure 57. Droplet velocity spectra of an XR8002 nozzle at 4 operating pressures, 50 cm below the tip.

Small droplets decelerate most because they have little momentum to fight the air resistance. They are now travelling only 2 to 4 m/s. The larger droplets are still travelling about 8 to 12 m/s. Increasing the spray pressure increases the droplets' velocity, but this effect is most pronounced for the larger droplets. Small droplets slow down quickly due to air resistance and do not benefit from higher initial velocities.

Conclusions may be drawn from these observations.

- Small droplets spend a lot more time getting from the nozzle to the target. As a result, they are more likely to be displaced by wind and start drifting. Also, the longer flight time means the small droplets are more exposed to atmospheric conditions that can cause evaporation, and many droplets evaporate completely before they reach the crop canopy.
- Larger droplets are less drift-prone because they have more momentum, the product of their velocity and mass. As such, they are also more likely to bounce off plant foliage.

Nozzle nomenclature

The nomenclature of nozzles provides for the identification of fan angle, flow rating, nozzle material and nozzle series.

Most manufacturers use similar systems for classifying their nozzles, but for simplicity, only the Spraying Systems format will be discussed here. For TeeJet nozzles, numbers stamped on the tip follow the following format: "**XR8002VS**."

Common designations of spraying systems flat fan nozzles

Leading letters	Interpretation	Features
XR	Extended Range	Maintains good spray pattern between 15 and 60 psi
DG	Drift Guard	Uses a pre-orifice design to emit a coarser spray at standard pressures and flow rates. Can be operated over pressures ranging from 30 to 60 psi
TT	Turbo TeeJet	Uses a swirl chamber and a flood jet design to create a wide angle coarse spray that can be operated over pressures ranging from 15 to 90 psi
TJ	TwinJet	Contains two orifices, one oriented slightly back, the other slightly forward, to produce a finer spray at a given flow rate
AI	Air Induction	Venturi-type nozzle uses air inclusion to produce a very coarse, low-drift spray between 40 and 100 psi
HSS	hardened stainless steel	Very wear resistant
SS	stainless steel	

Trailing letters	Interpretation	Features
VS, VH, VK, VP	VisiFlo colour coding and material identification	Colour coded nylon enclosing stainless steel (VS), hardened stainless steel (VH), ceramic (VK) and polymer (VP) tips. Colour identifies flow rating

The initial letters identify the nozzle series, which are manufacturer specific. In this example, the XR identifies the "extended range" tips. The next digits identify the fan angle when spraying water at 40 psi. In this example, an 80° angle will be produced. Other common angles are 110° and 65°. Wider angles produce finer sprays and permit the boom to operate closer to the ground without distorting the pattern. The last 2 or 3 digits identify the flow rating of the nozzle in US gallons of water per minute at 40 psi. In this case, 02 refers to 0.2 US gallons per minute.

Finally, the trailing letters identify the material of the nozzle. In "VS," the "V" refers to 'VisiFlo,' a plastic enclosure around the nozzle material that permits colour coding of nozzles and "S" to the stainless steel nozzle material. In the ISO colour coding system, orange identifies the 01 flow rating, green the 015, yellow the 02, blue the 03, red the 04, brown the 05, and so on.

Nozzle wear

Nozzle materials wear at rates that depend on the nozzle material and the nature of the spray liquid. Abrasive formulations such as wettable powders cause more rapid nozzle wear than liquid formulations. Ceramic provides the best wear characteristics of all materials. Plastic or polymer materials also have good wear characteristics. Stainless steel is less durable than some plastics. Brass is not durable and should not be used.

Measurement of droplet size spectra

All agricultural nozzles create a **polydisperse** spray (i.e., comprised of small and large droplets) that are difficult to describe using just one droplet size parameter.

There are several ways to describe the size of droplets in a spray. Three parameters are usually used together to get a more comprehensive picture of droplet size:

1. **Volume Median Diameter (VMD or $D_{V0.5}$)** – Drop diameter such that 50 per cent of total liquid volume is in drops of smaller diameter. Imagine that a representative sample of droplets in a spray is divided into two equal parts by volume, so one half contains droplets smaller than the VMD and the other half contains droplets larger than the VMD.
2. **Number Median Diameter (NMD or $D_{N0.5}$)** – Drop diameter such that 50 per cent of total droplet number is in drops of smaller diameter, without reference to volume.

Nozzle care
Clean nozzles carefully and observe nozzle patterns frequently. Replace nozzles with poor patterns or those whose output deviates more than five per cent from the average of the other nozzles on the boom.

3. **Proportion of total volume in droplets less than 100 μm** – If all the drops of a given spray were converted to a volume, then the proportion of the total volume in droplets less than 100 μm (or any other size class) could be determined. Since it is the small droplets that are most likely to drift, this parameter provides a quick reference to the drift potential of the spray.

Even a few large droplets can account for a large amount of spray volume; therefore, they can influence the VMD considerably. On the other hand, NMD is very sensitive to small droplets, which comprise the greatest number in a spray. The ratio of VMD to NMD can give an idea of the range of droplet sizes in a spray – the higher the number, the greater the range of droplet sizes. A VMD/NMD ratio of 1 identifies a spray with all the same droplet sizes.

The concept of VMD can be expanded to identify other aspects of the spray. For example, the $D_{V0.1}$ identifies the droplet size below which 10 per cent of the volume of the spray is contained, whereas the $D_{V0.9}$ identifies the droplet size below which 90 per cent of the volume of the spray is contained. These parameters can be used to describe the span, or range of droplet sizes, in the spray.

To simplify the description of agricultural sprays, a classification scheme has been developed in Europe that divides sprays into broad categories of coarseness. They are classified as *very fine*, *fine*, *medium*, *coarse*, or *very coarse* (Figure 58). This classification system has made labelling easier as product labels now state the spray quality for specific products. Spraying Systems has adopted the European system to help applicators make decisions about droplet size from various nozzles. As seen in Figure 59, the spray quality of nozzles at common pressures is now available. Other manufacturers will follow suit as the spray quality classification system is adopted in North America.
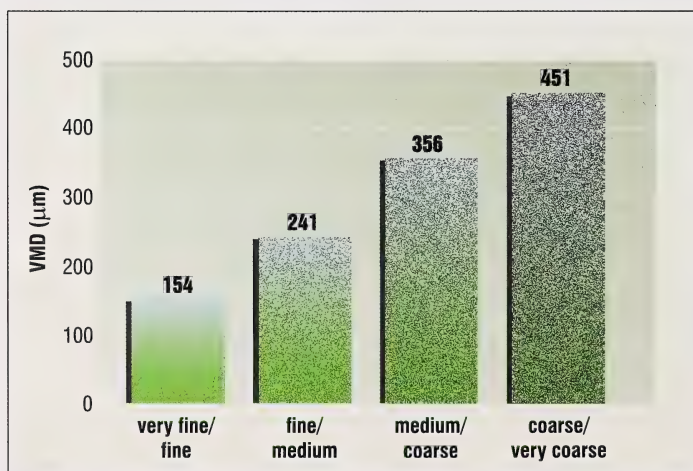
Figure 58. Size borders for classification of spray quality using the system developed by the British Crop Protection Council (BCPC). North America will be adopting this classification system in the future.   **Source 2**
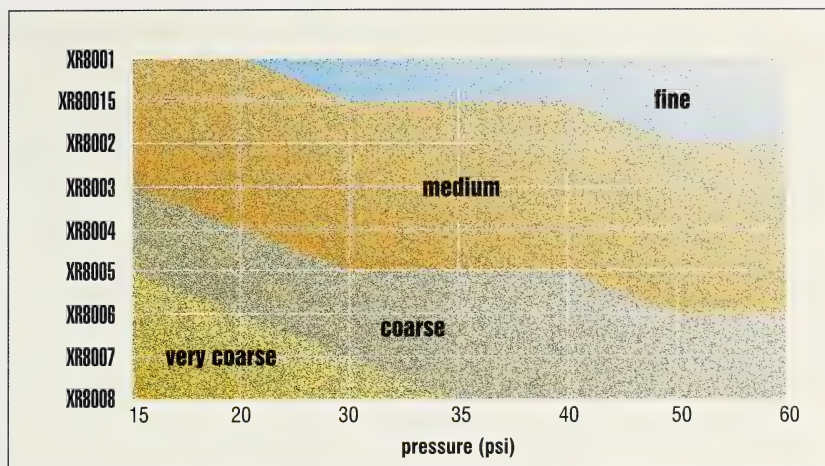
Figure 59. Effect of nozzle flow rate and pressure on BCPC spray quality produced by flat fan nozzles spraying water (courtesy of Spraying Systems, used with permission).   **Source 3**

Effect of nozzle type – For all nozzles, a higher volume output means larger droplet sizes. The table below shows that an 8001 tip has a VMD of about 140 μm and 20 per cent drift-prone droplets. These numbers change as the nozzle output increases, to a VMD of 225 μm and 6 per cent drift-prone droplets for an 8003. Therefore, higher carrier volumes usually result in less drift because they are commonly applied with a coarser spray. The spray solution is also more dilute at higher carrier volumes, contributing to less potent drift.

Droplet sizes for flat fan nozzles

Nozzle	NMD (μm)	VMD (μm)	% Volume <100 μm
XR8001	69	138	21
XR80015	78	175	10
XR8002	85	198	7
XR8003	85	223	6

Keeping the droplet size constant while changing carrier volume is difficult with off-the-shelf technology. The TwinJet (TJ), may help under some conditions. This nozzle uses two exit orifices, one oriented slightly forward, the other slightly back. If the spray quality from an 8004 may be too coarse, then using a TJ8004 will provide the spray quality of an 8002, at the 04 flow rate.

Effect of operating pressure – Nozzle pressure is a good way to change droplet size, but an inefficient way to change flow rate. Increasing the spray pressure decreases droplet size. Although droplets initially move faster when applied with a higher pressure, this effect dissipates very quickly. With higher pressures, all but the larger droplets will have returned to nearly the speed they would have travelled under a lower pressure (Figure 57). Therefore, higher pressures will not achieve better spray penetration from greater droplet velocities.

Flow rate is governed by a square root relationship with pressure. That is, to double nozzle output, pressure must be increased four times. To maintain a constant carrier volume, pressures need to fluctuate greatly in response to small changes in travel speed.

$$\text{flow 1}/\text{flow 2} = \sqrt{\text{pressure 1}}/\sqrt{\text{pressure 2}}$$

Effect of adjuvants – Spray adjuvants can have profound and often unpredictable effects on droplet size (see chapter on Adjuvants). In brief, adjuvants can alter the physico-chemical properties of the spray, and the most important of these are viscosity and surface tension.

Some adjuvants are specifically designed to increase droplet size, and they do so by increasing the **viscosity** (the ability of a liquid to resist flow) of the spray. The spray sheet becomes more stable, resisting breakup and extending further from the nozzle. The resulting droplets are larger and slower moving. Such sprays have a droplet size spectrum that is shifted toward larger droplets from conventional sprays, i.e., there are fewer small and more larger droplets, creating a less drift-prone spray.

Most **surfactants** (surface active agents) have the opposite effect. They primarily reduce surface tension, which decreases the stability of the liquid sheet emanating from the nozzle. The result is a finer spray. Surfactants differ in their effectiveness; some can be very dramatic while others can have little impact. Oils typically increase droplet size slightly, although responses differ from product to product.

The effects on droplet size are adjuvant specific and can also depend on which herbicide is mixed in the tank. For example, an adjuvant mixed with water may have an opposite effect on droplet size compared to when it is mixed with a herbicide. The important thing is to be aware of possible changes and take note before spraying. A coarse spray that is made more drift-prone by a surfactant can cause unpleasant surprises.

Effect of travel speed – Faster travel speeds have a shearing effect on the liquid sheet, creating instability and leading to a faster breakup. This outcome means smaller, more drift-prone droplets. Sprayers that travel at faster speeds use larger nozzles than slower sprayers do, to keep application volume constant. Although this method creates a less drift-prone spray, the effect is offset to a degree by the increased shear at the faster speeds. Aircraft operators are very aware of the role of shear on droplet size. Nozzles that point straight down expose the liquid sheet to the maximum amount of shear. Nozzles that point back avoid some of this shear, resulting in a coarser spray.

Other nozzles

Here are three of the numerous nozzle choices on the market:

1. Hollow cone nozzles – These nozzles use a swirl chamber that creates a cone-shaped pattern, which is hollow in the middle. The nozzles require higher pressures to operate properly and create a finer spray than equivalent flat fan nozzles. They are used primarily to apply fungicides and insecticides where such fine sprays provide a benefit.

2. Flooding type nozzles – Conventional flooding- or anvil-type nozzles were popular because they used a round orifice, which was less prone to plugging than flat fan nozzles. However, they have fallen out of favour for foliar applications because their patterns were erratic. Recently, a new flood jet design, the Turbo FloodJet, integrated a swirl chamber into the nozzle to correct the pattern problems. The new design emits a coarse spray that is suitable for drift-reducing application. These nozzles are also appropriate for soil-applied products, as droplet size is less important, and incorporation can compensate for somewhat erratic patterns.

3. Venturi nozzles – Some nozzles use a venturi design to create a vacuum that draws air into a mixing chamber. The spray droplets that leave the exit nozzle are very large and contain air bubbles. This spray is very drift-proof and can be used at higher-than-average pressures without becoming fine. The air-containing droplets are believed to be less prone to rebound, permitting low-drift spraying with little or no impact on efficacy.

Several types of these nozzles are available in Canada: the Greenleaf TurboDrop, and TurboDrop XL, the BFS Air Bubble Jet, the TeeJet Air Induction (AI), the Spraymaster Ultra, the Lechler ID and the Lurmark Ultra-lo Drift are the major brands of these nozzles available in Canada. A provincial factsheet (*Making Sense of New Nozzle Choices*) is available for further information.

Calibration and patternation

Proper spray uniformity is fundamental to accurate spray application. The goal is to apply the correct rate of crop protection agent (CPA) to the target area.

Calibration – Often, field calibration is done retroactively: after treating a field, the CPA or water used is divided by the area treated. If enough water and CPA were used up to treat the desired are, it is assumed that a certain amount of CPA per unit area was applied. While there is some use for this approach, it does not tell the applicator whether the application was done uniformly either across the field or along the width of the boom.

Before heading out to spray at the beginning of the season, an applicator should inspect the sprayer closely. Hoses, clamps and seals should be inspected for leaks or wear. Tank agitation should be verified. Filters should be examined and cleaned, and water should be flushed through the system. Flow regulators should allow for the desired range of operating pressures. The pressure gauge should accurately reflect pressure at the boom, not at the pump.

Spray uniformity
This process starts with measuring the correct amount of product, adding it to the correct amount of water and using a calibrated sprayer to apply it to the correct area.

To begin the calibration, fill the sprayer tank with clean water. Have the following equipment ready:

- notepad and pen
- stopwatch
- calculator
- plastic collection vessels to catch spray
- graduated cylinder(s)

The applicator should then take the following steps:

- make sure the correct nozzles are installed (do not mix and match different nozzle types)
- start the sprayer and bring the boom pressure up to 40 psi
- visually inspect the patterns of all nozzles and replace or clean those with poor patterns
- collect spray from each nozzle for a determined time, say 30 seconds
- measure the spray output using the same graduated cylinder, or compare the accuracy of graduated cylinders prior to calibrating
- express the average nozzle output from all nozzles in mL per min
- replace nozzles that deviate from this average by more than 5 per cent.

Now choices have to be made. If a certain carrier volume is desired, a simple formula can be used to calculate the speed necessary to apply that volume:

Formula 1

Calculate travel speed required for a fixed spray volume (assuming 50 cm nozzle spacing).

Formula: Speed (km/h) = average nozzle output (mL/min) *1.2 / desired volume (L/ha)

Example: If the sprayer is equipped with 8002 nozzles, average nozzle output may be about 700 mL/min. Assume an application volume of 100 L/ha:

700 *1.2 / 100 = 8.4 km/h

If a certain speed is required, the application volume at that speed must be calculated:

Formula 2

Calculate spray volume for a fixed travel speed.

Formula: Volume (L/ha) = average nozzle output (mL/min) *1.2 / desired speed (km/h)

Example: If the sprayer travels at 9.1 km/h then:

700 *1.2 / 9.1 = 92 L/ha

Sprayer speed must also be calculated:

Formula 3

Calculate travel speed. It is best to drive a fixed distance and record the time required.

Formula: Speed (km/h) = distance travelled (m) / time required (s) *3.6

Example: If it takes 20 s to travel 40 m

40 / 20 *3.6 = 7.2 km/h

Even if an automatic flow rate controller is used, the output from each nozzle should still be measured to identify problems along the boom. **There is no substitute for this important step!** A few calculations will help verify that the monitor is functioning properly.

Patternation – Even if an applicator calibrates the sprayer properly, poor uniformity can still occur for several reasons: if the boom height is improperly adjusted, through excessive boom sway, by using certain adjuvants or by spraying in windy conditions. A poor pattern will result in over-application in some areas and under-application in others, which may reduce weed control or increase crop damage.

Poor application patterns are often masked by high herbicide rates; the applicator is unaware of the poor patterns because the herbicide rate is high enough to cover up for mistakes. For lower rates, application accuracy becomes more important.

During calibration, spray patterns are inspected visually, which is a good start but may not be a foolproof way to ensure a good spray pattern. To verify a good pattern along the boom, a patternator must be used. A patternator can observe more subtle changes in pattern. This tool is a flat piece of plastic with channels cut into it to collect spray from incremental regions of the pattern (Figure 60). The patternator is held in place under the nozzles until enough liquid has accumulated in the channels to give a visual indication of the transverse volume output distribution. These tests are appropriate to identify worn nozzles or the wrong boom height. Data from these tests are used to calculate the coefficient of variation, or CV, for a set of nozzles.
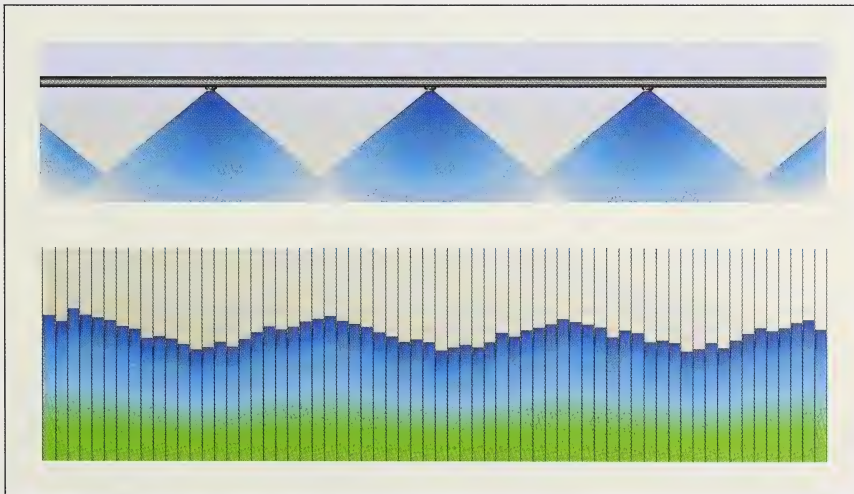

Figure 60. A typical static spray pattern.

By definition, the CV = s/$\overline{X}$ *100, where 's' is the standard deviation of the spray volume in the patternator channels and '$\overline{X}$' is the mean volume in the patternator channels.

As a guideline, if the coefficient variation (CV) exceeds 15 per cent, then the pattern is considered to be unacceptable.

When a sprayer travels through a field, the air turbulence, boom sway and bounce can further distort patterns. As a result, variability increases in the field, but it becomes difficult to measure.

To give some examples of variability in the field, consider that a static CV of 10 per cent may increase to 20 per cent just by moving the boom through air. Higher wind speeds and faster travel speeds further increase CVs. For example, application with a tractor-drawn sprayer travelling at 8 km/h resulted in CVs of about 12 per cent, whereas application with a self-propelled sprayer travelling at 32 km/h resulted in CVs of 20 per cent. Faster wind speeds also increase deposit variability. On plant leaves, spray deposit CVs usually exceed 50 per cent and can be as high as 150 per cent.

Effect of nozzle type and condition – New nozzle designs have improved pattern uniformity. Among flat fan nozzles, the XR series provides good patterns between 15 and 60 psi at 45 cm above the target. The TT series provides an ever-wider range of operating pressures (from 15 to 90 psi) and, therefore, suits operations with automatic rate controllers. Older nozzles, especially those made with brass, are prone to wear and deformation, distorting patterns and changing output. Stainless steel, polymer or ceramic materials should be chosen to delay the onset of these problems. Hollow cone nozzles provide poorer patterns than flat fan nozzles, especially at lower pressures. Venturi nozzles require higher pressures to achieve good patterns.

Finer sprays are more at the mercy of atmospheric conditions for their deposition. As explained earlier, a large droplet will tend to travel in the direction in which it was released whereas a small droplet is more likely to be displaced from its flight path and deposited elsewhere. The prediction of flight and deposition patterns of small droplets becomes impossible. Fine, low volume sprays often have more erratic deposit patterns, which can result in variable results.

Effect of adjuvants – Spray adjuvants can dramatically affect spray patterns. The addition of a surfactant often widens the fan angle of a nozzle pattern and creates finer sprays. Thickening adjuvants can narrow the spray pattern, creating improper overlaps and introducing streaks. Before using a new adjuvant, applicators should take the time to observe the pattern and make adjustments to spray pressure, boom height and nozzle type to ensure correct application.

Transport to Target

After ensuring the CPA in question is applied as uniformly as possible, the next goal is to have it encounter the target plant or animal and be retained. Spray interception and retention are very complex, and researchers are still working to understand how these processes are governed and how they can be influenced.

Droplet dynamics

Physicists who study atomization and spray cloud behaviour have developed laws and equations to describe how droplets move in the atmosphere. Many of these principles reveal interesting and surprising characteristics. For example, when calculating the minimum spray volumes required to achieve a certain spray coverage, the merits of fine sprays become clear. Small droplets are able to provide a density of 1 droplet per mm^2 of flat target surface at less than 1 L/ha, whereas a coarse spray may require hundreds of litres for the same coverage. See table below.

Theoretical droplet densities and carrier volumes

Droplet diameter (μm)	Volume required (L/ha) for density of 1 droplet/mm^2 on a flat surface	Droplet density/mm^2 when applying 1 L/ha evenly over flat surface
10	0.005	191
20	0.042	23.9
50	0.655	1.53
100	5.24	0.19
200	42	0.024
500	655	0.002

Source 4

Although fine sprays provide excellent coverage, they evaporate rapidly and drift easily. Droplets less than 50 μm can evaporate so quickly that they will often disappear just before or soon after impact with the target. See table below.

Theoretical lifetimes and corresponding fall distances of droplets under two atmospheric environments.

	Temp (ºC) 20 RH (%) 80		Temp (ºC) 30 RH (%) 50	
Droplet diameter (μm)	Lifetime to extinction (s)	Fall distance (m)	Lifetime to extinction (s)	Fall distance (m)
10	0.56	0.09	0.16	0.02
50	14	0.5	4	0.15
100	57	8.5	16	2.4
200	227	136	65	39

RH = relative humidity

Source 5

The stop distance measures the distance that a droplet requires to adjust itself to the surrounding airstream. The table below shows how small droplets slow down very rapidly in still air. A 50 μm droplet released at 50 m/s needs only 37.5 cm to slow down to its terminal velocity. Only droplets greater than 100 μm are able to maintain their momentum for a significant distance. When small droplets slow down to their terminal velocity in still air, gravity has little effect and they move slowly, essentially going wherever the wind blows them.

Terminal velocity, fall time and stop distance of various droplet sizes

| Droplet diameter (μm) | Terminal velocity (m/s) | Fall time from 3 m | Stop distance (cm) | |
			Initial velocity = 1 m/s	Initial velocity = 50 m/s
10	0.003	16.9 min	0.03	1.50
20	0.012	4.2 min	0.12	6.11
50	0.075	40.5 s	0.75	37.5
100	0.279	10.9 s	2.45	123
200	0.721	4.2 s	7.35	367
500	2.14	1.7 s	21.8	1091

Source 6

Impaction and Retention

Impaction

When spray droplets encounter an object like a plant leaf, the first question is whether they will strike this object or not. The orientation of the leaf, the relative size of the spray droplets and the leaf as well as the trajectory of the spray all have to be considered.

Droplet size information makes clear that there are relatively few large droplets in most sprays. As a result, the chance of an encounter with any object is much less for large droplets compared to the much more abundant small droplets. Based on probability, large droplets are less likely to hit an object than small droplets. However, the larger the leaf, the greater the likelihood that a large droplet will encounter it. Overall, fine sprays are preferred when targeting small objects (grasses, insects), and coarse sprays are preferred for targeting large objects (broad-leaved plants).

The **capture efficiency** of the leaf is also important. Air flows around all objects and must change direction to get around the object. For a large leaf, the air's path around it is longer, and its change in direction is greater than for a small leaf (Figure 61). A small droplet, which has little inertia of its own, will follow the air movements around the leaf and may never strike it. A large droplet, with sufficient momentum to overcome the air flow, penetrates the flow and hits the leaf.
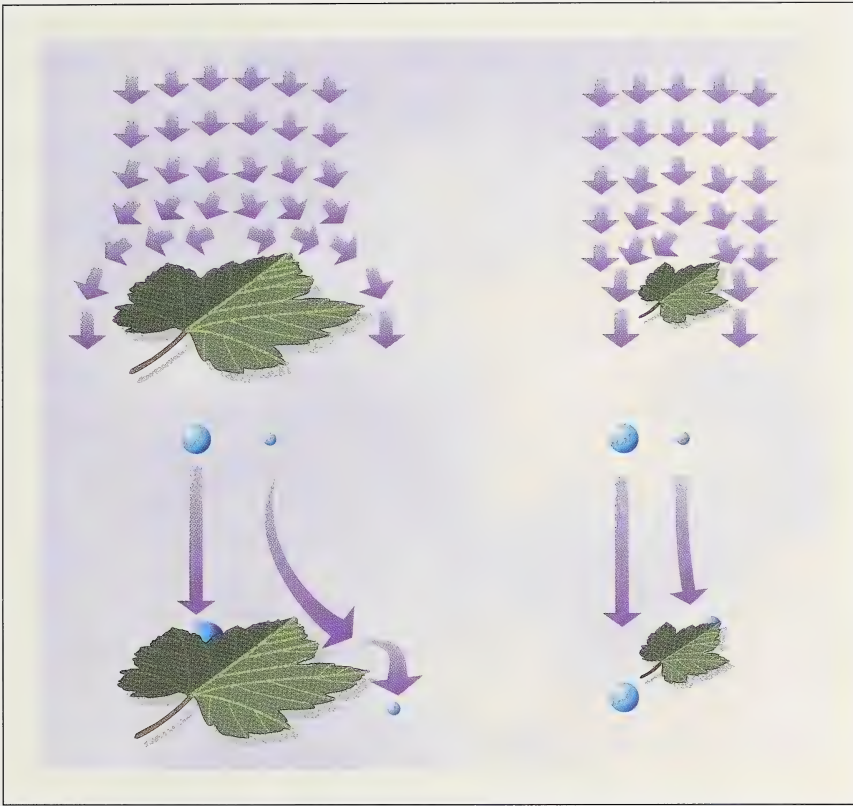
Figure 61. Spray collection efficiency: top, air flow around large and small leaves; bottom, droplet movement around same leaves.

The flow of air around a small leaf or stem changes less than for a larger object, and a small droplet can still hit the target. Considering collection efficiency alone, small targets like stems, petioles or small leaves are much more likely to capture small droplets than large leaves. If large leaves are the target, larger droplets provide greater efficiency.

Droplet velocity is also important for determining spray interception. Since a small droplet does not have the momentum to overcome the change in direction imposed on it by the air flowing around a large object, accelerating the droplet can make a difference. In this way, air assist can effectively increase spray capture. But air assist has to be used carefully. Too much air can accelerate the droplets to such a degree that they will simply bounce off the leaves.

The trajectory of the spray can be influenced by nozzle orientation, nozzle fan angle and travel speed. A more vertical spray trajectory will favour targets that are perpendicular to the droplet stream, such as broad-leafed leaves. When the spray is oriented more in the horizontal (by tilting the nozzles forward or travelling faster),

then vertical targets such as plant stems and the leaves of grassy weeds will be favoured. These factors interact strongly with droplet sizes, so it is difficult to make predictions.

Retention

Once the spray reaches the target, it must be retained to have an effect. Spray retention is governed by two opposing forces:

1. the energy contained in the incoming droplet
2. the ability of the droplet/target interface to dissipate the energy and prevent the drop from rebounding

The critical factors for retention are droplet kinetic energy (a product of droplet size and the square of its velocity), dynamic surface tension of the droplet and leaf surface characteristics. Large and faster droplets will contain more energy, which will need to be dissipated on impact. A leaf surface considered to be **easy-to-wet** (i.e., a water droplet will spread somewhat on such a surface) will retain a large variety of droplet sizes. Even sprays of pure water will stick to pigweed and smartweed, for example.

In contrast, sprays resist adhering to surfaces that are **difficult-to-wet**, such as green foxtail, wild oats and kochia. Fine sprays are more easily retained on such surfaces (Figure 62). The addition of surfactants can increase spray retention, but not all surfactants behave the same way.
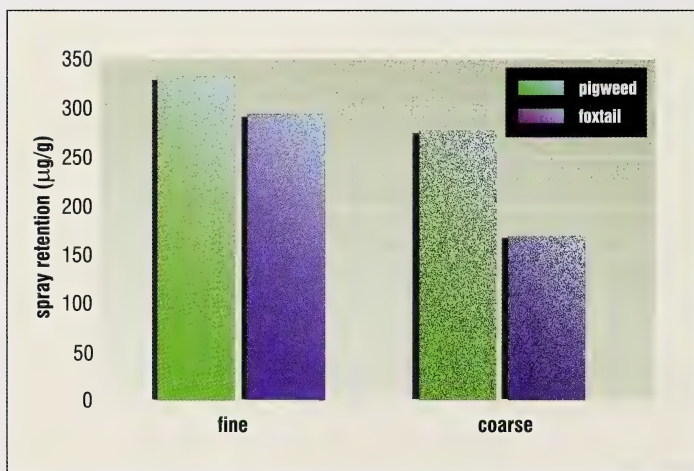
Figure 62. Effect of droplet size on spray retention by a difficult-to-wet weed (foxtail) and an easy-to-wet weed (pigweed).

Canopy penetration

Crop canopies are a mix of stems and leaves of various sizes, pointing in many directions. Canopy penetration is difficult to improve, but in general, a more vertical spray orientation will provide the greatest likelihood of penetrating a canopy. This result can be achieved by orienting nozzles downward and reducing travel speeds.

When spraying into a no-till canopy comprised of standing wheat stubble, the best penetration was obtained with a coarse spray (Figure 63). When the spray was angled 45° forward, the stubble intercepted a greater proportion of the spray. Increased droplet velocity is also of value, and this increase is best achieved with air assist. Research has demonstrated that air assist is well suited for increasing mid-canopy coverage.
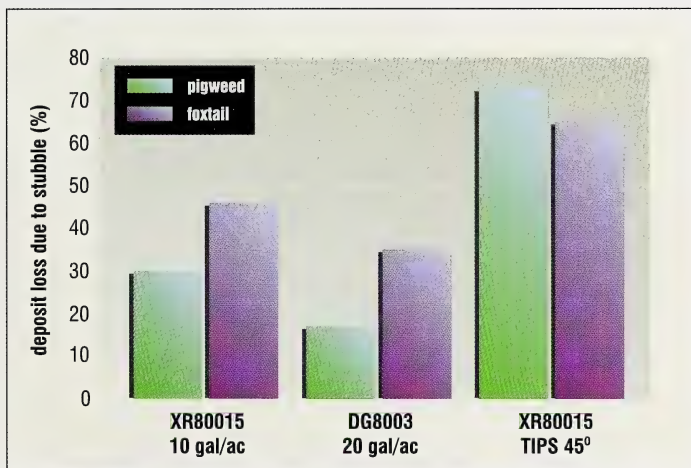
Figure 63. Loss in spray deposit quantity due to standing wheat stubble with three application techniques and two weed species.

Overall, spray penetration is an application of the principles governing spray interception (i.e., collection efficiency) and is a matter of relative droplet and canopy size. For a mature canola canopy, the large, horizontally-oriented leaves create primary interference. The previous discussion on spray interception suggests that large droplets will likely be intercepted by such objects, whereas small droplets are more likely to go around them. As a result, a fine spray better penetrates such a cascading layer of horizontal objects. For a more vertically-oriented canopy, such as a cereal, a coarser spray will have a greater chance of avoiding contact with the narrow leaves, which are pointed up or down. Some dense canopies are very difficult to penetrate and may require the use of drop tubes to position the nozzle closer to the target.

Deposit Formation

Once the spray is retained by the target plant, it makes contact with the leaf surface and spreads and dries within a few minutes. The nature of this deposit can have a profound impact on how effective the product will be.

For example, consider a contact herbicide applied at a rate of 1000 g/ha in 100 L/ha water. This results in a dose of 10 μg in 1 μL per cm^2 of land area. An individual lamb's-quarters plant at the 4-leaf stage might have a projected leaf area of 10 cm^2 and, assuming it captures all incoming spray, would receive a dose of 100 μg in 10 μL.

Now consider two extreme cases: in the first, the entire dose is transferred in 4 single droplets of 1700 μm diameter each, 1 on each leaf (total volume = 10 μL). In the second case, the dose is delivered in 20,000 droplets with 100 μm diameter each uniformly to the entire plant (total volume = 10 μL). Which deposit would you expect to provide greater effectiveness?

The answer seems obvious, but it is actually a closer contest than one might think. The fine spray would certainly provide superior coverage, but it would also evaporate very rapidly and provide only a short time-frame for uptake. In addition, each droplet would contain only a very small amount of active ingredient, perhaps not enough to cause a toxic effect to the cells underneath. The coarse spray would provide less coverage, but the deposits would stay in liquid form longer and provide more active ingredient per unit leaf area, increasing the likelihood of uptake and cell death. As with the entire dose transfer process, compromises must once again be made to achieve optimal results under a variety of conditions.

High evaporation rates associated with hot and dry weather conditions will place finer spray deposits at a disadvantage compared to coarser sprays. Systemic products will likely be less sensitive to spray deposit structure than contact products. And leaf surface structures of different weeds may provide an advantage to some types of deposits.

What kind of spray deposit?

Researchers are still struggling to define the ideal spray deposits for herbicides, and only a few guiding principles have been established. Research results show that the ideal droplet size varies from herbicide to herbicide and from weed to weed. Some contact herbicides perform very well when applied in small droplets, whereas others may not work as well. For glyphosate, carrier volume is more important than droplet size. In general, droplet size effects become more important at lower carrier volumes, and smaller droplets often perform better with lower volumes.

Researchers now believe that the kinds of sprays delivered by hydraulic nozzles ensure that a variety of droplet sizes are always present to accommodate a range of needs and, thus, offer a good compromise spray. Crop canopies are so complex that no one can predict which droplet size will penetrate most effectively over a range of conditions. Once deposited, a combination of large and small droplets that provide both rapid and

slow drying as well as high and low concentrations of active ingredient per unit area often provide optimal efficacy characteristics.

The increased use of low-drift nozzles and high clearance sprayers has raised the question of the consequences of applying generally coarse spray to control pests. Although coarse sprays have historically been thought to detract from pest control, newer technologies such as air-induction nozzles may challenge these views.

The droplet size distributions (by volume) of an XR11002 and a TT11002 tip, both operated at 40 psi, can be used to illustrate expected effects of coarser sprays (Figure 64). The XR tip has a greater proportion of its volume output in smaller droplets (<100 μm) than the TT tip (16 vs. 5%). This makes the XR spray more drift-prone, but also provides more smaller droplets for better coverage. The TT tip has more volume in the larger droplets (>400 μm), possibly hurting spray retention (14 vs. 2%). The net result of these differences will depend on environmental conditions, target properties, the active ingredient, and other factors.
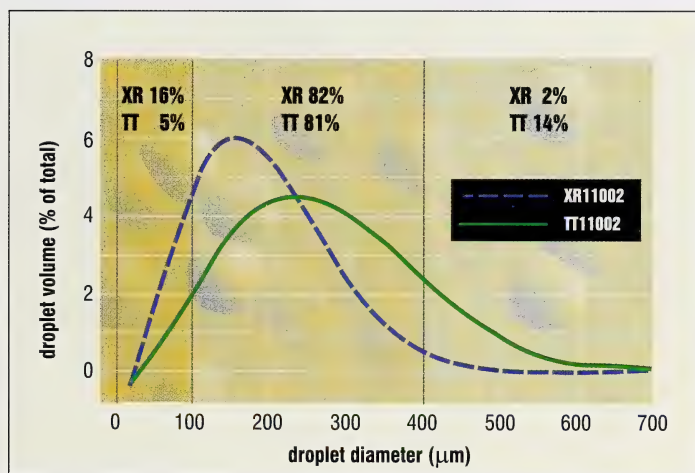
Figure 64. Changes in droplet size spectra from a conventional spray to a low-drift spray. What are the consequences for weed control?

Applicators should not expect a single nozzle to optimize all spray operations. Atmospheric conditions, the nature of the weeds targeted and the active ingredient can all influence which nozzle should be chosen. A balance between effectiveness and off-target impact must always be sought. At times, a fine spray may be most appropriate (i.e., fungicide and insecticide applications), whereas a coarser spray may be needed to control drift or enhance cereal canopy penetration. The applicator must be sufficiently trained to make the correct decision for each situation and always use the best application method for the job.

Summary of effects of changes in application technique on droplet size and spray behaviour.

Factor	Effect on			
	Droplet size	Spray retention and coverage	Drift	Canopy penetration
Increased Spray Pressure	Finer spray	Usually improved	More	No effect
Faster Travel Speed	Somewhat finer spray	Little effect	More	Less for vertically oriented canopies
Higher Boom Height	Finer at target	Little effect	More	Reduced
Coarser Spray	Coarser	Reduced on difficult-to-wet species	Less	Improved for vertically-oriented canopies
Air Assist	Depends on system, usually finer	Usually improved	Depends on canopy density and airblast strength and direction	Usually improved to mid-canopy
Electrostatics	Depends on system, usually finer	Usually improved, often dramatically	Depends on canopy and other factors, usually more	Usually little effect, although upper canopy will obtain greater dose
Lower Carrier Volume	Usually finer spray	Usually improved	More	Reduced for vertically-oriented canopies
Off-label Adjuvant	Depends	Depends	Depends	Depends

Movement In/on Plant

Most events after spray deposition are not under the direct influence of the applicator and will not be covered in detail here. Although spray redistribution on the plant can be a function of carrier volume and formulation, most events such as photodegradation and rainfastness are primarily controlled by the chemistry and formulation of the active ingredients. Aspects relating to herbicide uptake and translocation are covered elsewhere in this book.

Adjuvants

- any ingredient added to a spray solution that changes its characteristics is called an adjuvant
- adjuvants can reduce foaming, increase spreading, enhance uptake, reduce drift and perform other roles
- adjuvants are product-specific and cannot be easily substituted

Adjuvants: Definitions and Function

Adjuvants are defined as any substance in a herbicide formulation or added to the spray tank to modify biological activity or application characteristics. Currently, adjuvants are playing an increasingly important role in the application of herbicides. There are, overall, a bewildering array of adjuvants and terms to describe their function.

Adjuvants can be broadly classified in two categories (see table below):

- activators and spray modifiers
- utility modifiers.

Activators and spray modifiers are intended to improve the biological performance of the pesticide by modifying physical or chemical characteristics. Utility modifiers do not directly improve efficacy, but widen the condition under which a product is useful.

An introduction to adjuvants

Because of the specific way adjuvants affect spray atomization, deposition and uptake, it is impossible to predict how any one adjuvant will interact with the many factors that govern weed control without extensive experimentation. As a result, it is important to follow label recommendations to ensure reliable product performance.

Adjuvants are useful tools to ensure or enhance the activity of herbicides, and as a result, they are frequently included in product formulations or recommended on product labels.

Classification of adjuvants

Adjuvant type	Examples	Purpose
Activators and spray modifiers	surfactants	lower surface tension enhanced droplet spread
	crop oils, crop oil concentrates	enhanced uptake
	stickers, spreaders	film forming, rainfast
Utility modifiers	buffering agents	enhance solubility
	anti-foamers	reduce foam buildup
	compatibility agents	enhance mixing
	drift control agents	increase droplet size

Surfactants

One category of adjuvant type is the surfactants. A surfactant (surface active agent) is defined as "material that improves the emulsifying, dispersing, spreading, wetting or other properties of a liquid by modifying its surface characteristics."

Surfactants must be added to spray solutions when the herbicide formulation contains too little or no surfactant on its own. Or, they are added when application rates or volumes dilute the surfactant in the formulation to such a degree that additional surfactant is needed to raise the concentration to its intended level. Surfactants are **very specific in their effects**, so it is important to follow label directions to avoid failures.

Surfactant registrations with herbicides (data limited to Western Canada)

Trade name	Type	Herbicides
Agral 90	non-ionic	Ally, Amber, Escort, Muster, Pursuit, Refine Extra, Reglone, Roundup, Telar, Touchdown
AgSurf	non-ionic	Ally, Amber, Escort, Muster, Pursuit, Refine Extra, Reglone, Roundup, Telar, Touchdown
Citowett Plus	non-ionic	Ally, Amber, Basagran (peas), Escort, Muster, Refine Extra, Telar
Companion	non-ionic	Ally, Amber, Laredo, Muster, Refine Extra, Renegade, Roundup, Telar, Victor, Wrangler
Enhance	blend	Roundup
Frigate XL	ionic	Roundup, Touchdown
LI 700	non-ionic	Laredo, Renegade, Roundup, Victor, Wrangler
Rely	ionic	Touchdown
Super Spreader Sticker	non-ionic	Ally, Amber
Surf 92	non-ionic	Pursuit
Tween 20	non-ionic	Krenite

Crop Oil Concentrates (COC's) are vegetable or petroleum oils. Their primary function is to enhance the uptake of a herbicide into the plant. COC's contain surfactants to help the oil mix with water. Many grass herbicides are mixed with crop oil concentrates specifically designed for that herbicide and are packaged with it.

Crop oil registrations with herbicides (data limited to Western Canada)

Trade name	Herbicide
Assist	Basagran (all crops), Laddock
Bioveg	Bladex Nine-T
CanPlus 411	Assure
Sure-Mix	Assure
Crop oil or corn oil	Atrazine
Score	Horizon
Amigo	Select
Merge	Poast
Prevail C	Prevail
Turbocharge	Achieve, Affirm, Venture 25 DG

Other groups of adjuvants

Spray modifiers and utility modifiers are less common than activators in Canada. Among the spray modifiers are spreaders and stickers, which enhance spray retention and adhesion and also prevent wash-off by rain. Utility modifiers include buffering agents, defoamers, compatibility agents and drift control agents. Buffering agents are sometimes needed to enhance the solubility of an active ingredient (e.g. "acidulate" for Assert). Drift control agents are used to increase the droplet size of sprays and are mandated for some applications in the US, but are not yet widely used in Canada.

While it is true that adjuvants are designed to enhance herbicide performance, there is no universal adjuvant, and any given product can increase, decrease or have no effect on performance. In addition, the sheer number of products on the market defies anyone trying to make sense of them all. In the US, there are hundreds of registered adjuvants and very few standards of nomenclature or performance. In fact, there is no end to the names given to adjuvants, many of which do not really describe what kind of performance to expect.

Why the confusion about adjuvants?
One reason people are confused about adjuvants is that there is so little useful information available. Anecdotal accounts of how an adjuvant boosted efficacy are often heard, but few details are provided.

Some names for adjuvants		
acidifier	dispersant	soap
activator	drift reducer	solubilizer
additive	emulsifier	spreader
antifoamer	esterified seed oil	sticker
attractant	evaporation reducer	surfactant
buffer	extender	synergist
chelating agent	fertilizer	thickener
compatibility agent	humectant	translocator
conditioner	inert methylated seed oil	uv protectant
coupler	neutralizer	vegetable oil
deposition agent	penetrator	wetter
detergent	saponified seed oil	

Many US adjuvants were developed for a single herbicide and required no efficacy testing to be registered. As a result, there is no way to predict how well a product will perform either with a different herbicide, on different weeds or under different environmental conditions without conducting experiments.

In Canada, an adjuvant claiming to enhance efficiency must be tested with the product for which it is recommended, and efficacy data must support its registration. For that reason, most herbicides have only one specific adjuvant registered for use or a few generic products at most.

How Surfactants Work

Surfactants affect the following spray characteristics or processes:

- surface tension
- atomization
- spray retention
- evaporation and persistence
- deposit formation
- cuticle penetration

Surface tension

What is surface tension? The answer is somewhat complicated. Liquids have a tendency to assume a low-energy state, which is when surface area is minimized (i.e., the liquid has a spherical shape). Energy must be supplied to increase this surface area. The amount of energy necessary to increase the surface area of a liquid by a unit amount is known as its surface tension.

Surfactants are primarily known for their ability to reduce the surface tension of a spray solution.

104

Water, by itself, has a high surface tension because water molecules are very attracted to each other. Inside the droplet, this strong cohesion is balanced in all directions. At the outer edge of a droplet, the strong attractions are unbalanced – there is more pull toward the middle than there is toward the outside. This imbalance of forces causes the droplet to try to maintain a spherical shape.

Surfactant molecules have the properties of both water and oil. One end of the molecule is water-loving (hydrophilic) and the other is oil-loving (lipophilic) (Figure 65). When added to water, surfactant molecules mix and replace water's very cohesive bonds with less cohesive bonds between water and surfactant. As a result, the imbalance of forces is reduced, and less energy is required to deform the droplet.
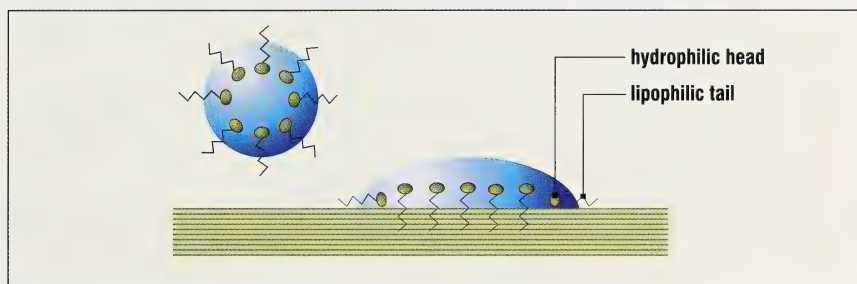
Figure 65. Interaction of hydrophilic and lipophilic parts of surfactant molecule with water and a waxy leaf surface.

A surfactant-containing droplet can interact with other surfaces because of the hydrophilic and lipophilic nature of the surfactant molecules. If a droplet sits on a waxy leaf surface, the surfactant is able to form a bridge between the water and the wax. The lipophilic parts of the surfactant interact with the wax, and the hydrophilic parts interact with the water in the solution. As a result, the droplet has better contact with the leaf surface and can spread.

The degree to which a droplet spreads can be described by the "contact angle," the angle between the leaf surface and the leading edge of the droplet (Figure 66). This parameter varies widely among plants species, plant age, location on the leaf and so on. Contact angles are at their greatest for difficult-to-wet plants and smallest for easy-to-wet plants.
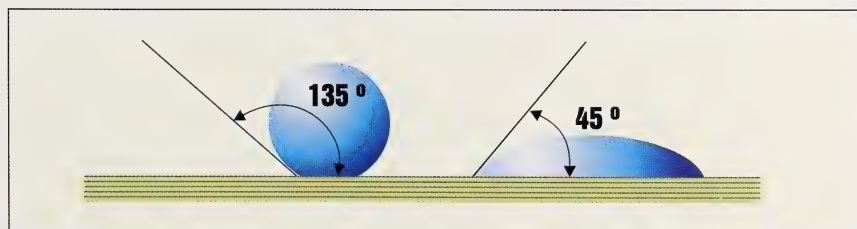
Figure 66. Contact angle of droplets on a difficult-to-wet leaf surface without and with surfactants.

To minimize surface tension, the surfactant molecules must be evenly dispersed through the liquid and have their hydrophobic and hydrophilic regions in proper alignment with the water molecules. Most surface tension data are for the "static" case, that is for a spray liquid at rest or equilibrium. Under static conditions, minimum surface tension is achieved at the "critical micelle concentration," usually about 0.1 per cent by volume (Figure 67).
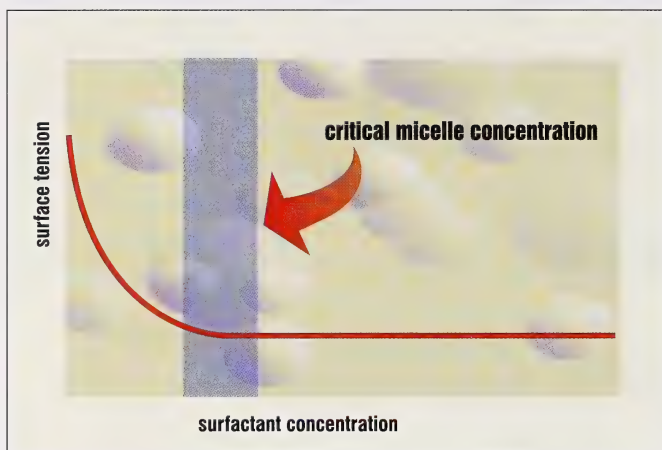
Figure 67. The critical micelle concentration (CMC) is the concentration of surfactant in a liquid, which minimizes the static surface tension.   **Source 7**

Atomization

The use of adjuvants profoundly affects the physico-chemical properties of a spray solution, including viscosity and dynamic surface tension. These properties also play a role in spray atomization. In general, lower surface tensions and viscosities create finer sprays, whereas visco-elasticity can affect droplet rebound.

When a comparison of the atomization of water, an organosilicone surfactant and a drift retardant was made using a XR8003 nozzle at 40 psi, dramatically different droplet size spectra were obtained. The surfactant-containing spray was finer than plain water, and the drift reducing spray was much coarser (Figure 68). Adjuvants can therefore significantly affect spray drift.

Always consider the effects of any adjuvant on spray atomization, which has important consequences for spray drift, retention and evaporation.

106

Figure 68. Droplet size spectra of water, surfactant and spray thickening, drift-reducing adjuvant sprayed through an XR8003 tip at 40 psi.

The droplet velocities of these sprays also differed – higher velocities were obtained for the surfactant spray, with the lowest velocities for the drift-reducing spray (Figure 69). The impact of droplet velocity is less important than that of droplet size, although some effects could be observed. For example, faster-moving small droplets are less likely to drift than their slower counterparts, and faster-moving large droplets are more likely to bounce off leaves.
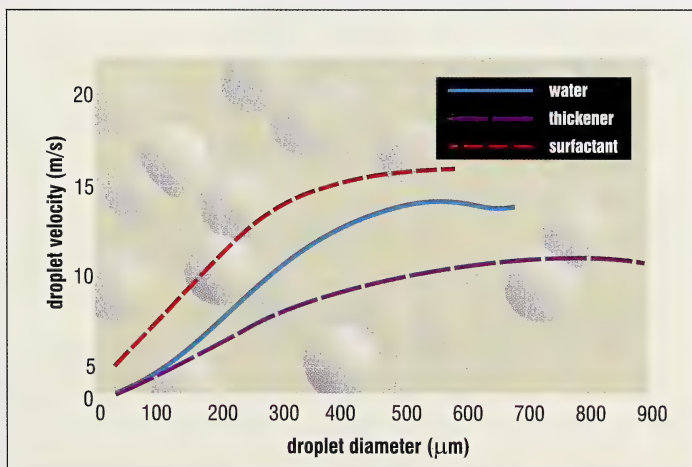
Figure 69. Velocity spectra of water, surfactant and spray thickening drift-reducing adjuvant sprayed through an XR8003 tip at 40 psi.

Spray retention

The use of surfactants may be necessary to obtain good spray retention on some leaf surfaces. Generally, weeds that are difficult-to-wet benefit more from surfactant inclusion than ones that are easy-to wet. For difficult-to-wet leaves, spray retention is virtually impossible to achieve without a surfactant, whereas for easy-to-wet leaves, the additio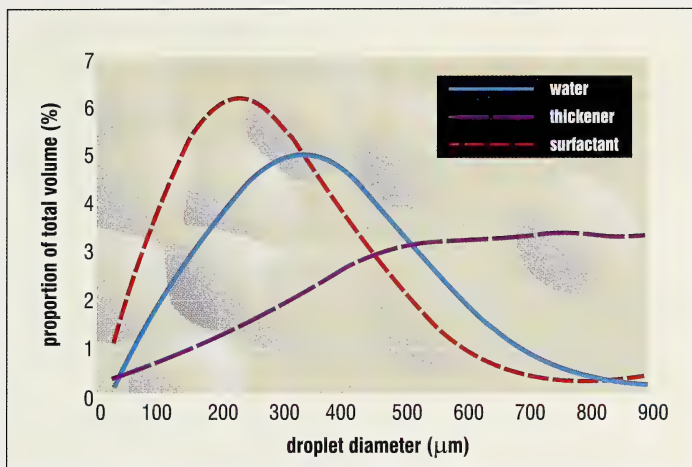n of a surfactant can lead to earlier runoff. Intermediate degrees of wettability usually give the highest retention values.

Wetting is affected by the structure of the leaf – including the presence of hairs, hair density and the micro-structure of the cuticle. It is usually the type of wax, not its quantity, that affects retention. Poor spray retention has been associated with micro-rough wax layers, which trap air on contact with a droplet and prevent good adhesion.

There is a limit to what surfactants can do to enhance retention. In droplet bounce studies, neither small nor large water droplets could be retained by foxtail leaves. When surfactant was added to the spray solution, small droplets could be retained by foxtail, although larger droplets still tended to bounce off.

In spray retention studies, the effect of leaf type was demonstrated by applying a water spray and a surfactant-containing spray to corn (difficult-to-wet) and velvetleaf (easy-to-wet). Surfactant greatly enhanced the spray retention on corn, but had only minor effects on velvetleaf (Figure 70). An understanding of the nature of the weed target is needed to predict the effect of adding a surfactant.
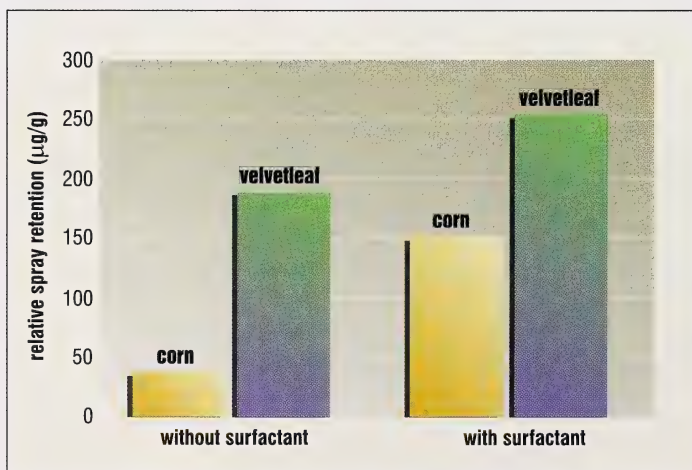
Figure 70. Effect of a surfactant on spray retention by corn (difficult-to-wet leaves) and velvetleaf (easy-to-wet) leaves.

108

Evaporation and persistence

After a deposit has formed, it is subject to environmental conditions that can dramatically reduce its effectiveness. Some adjuvants form oily films on plant leaves, which reduce evaporation of the water carrier, increase rainfastness or offer protection from UV radiation. As a result, the active ingredient uptake is prolonged.

Adjuvants differ in their effect on evaporation; some reduce these losses whereas others have no effect at all. Adjuvants that cause the spray deposit to spread dramatically may have counteracting effects. While spreading increases the area of contact with the leaf, it also increases evaporative and photodegradative losses, which may hurt uptake. As in other areas, effects may be counteracting, and a balance between positive and negative effects must be struck to achieve the desired result.

Deposit formation

Good weed control relies on the formation of a deposit that is efficiently taken up by the plant surface. When a droplet lands on a leaf, the water rapidly evaporates, leaving the non-volatile ingredients on the leaf surface. Because herbicide uptake is driven by diffusion, it is much easier for a liquid to diffuse across a barrier than for a dry crystal. Adjuvants can affect how the deposit forms, either keeping it in an amorphous liquid-like state or causing it to crystallize (Figure 71). Although the processes are not well understood and there are exceptions, it is thought that the amorphous-type deposits are preferred for most herbicides.

Physiology of Herbicide Action by Devine/Duke/Fedtke, © 1993. Adapted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

drying

amorphous, hydration sheath
good uptake

crystalline, no hydration sheath
limited uptake
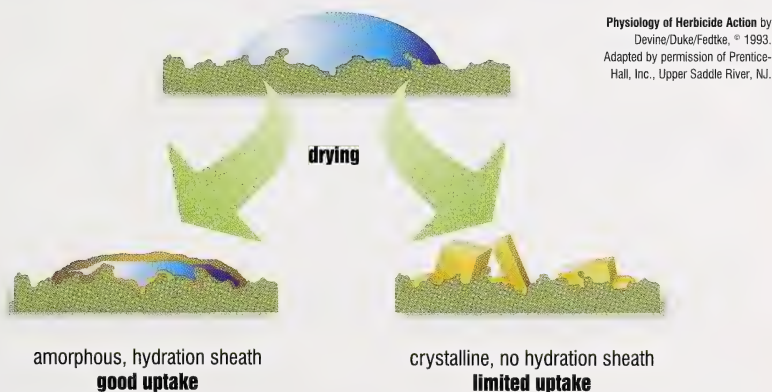
Figure 71. Upon drying, spray droplets can form amorphous deposits surrounded by a hydration sheath, which provides a route of uptake into the plant (left), or a crystalline deposit, from which active ingredients have a much harder time penetrating.

Cuticle penetration

The most important barrier of herbicide entry into the leaf is the leaf cuticle, a layer of waxes the plant uses to protect itself from the environment (Figure 72). This waxy layer is composed of films or deposits that resemble rods, spheres, cubes or platelets, depending on the species and age of the plant. Wax builds up in response to environmental conditions during the plant's development, and as might be expected, more waxes are deposited under sunny, dry and hot conditions.
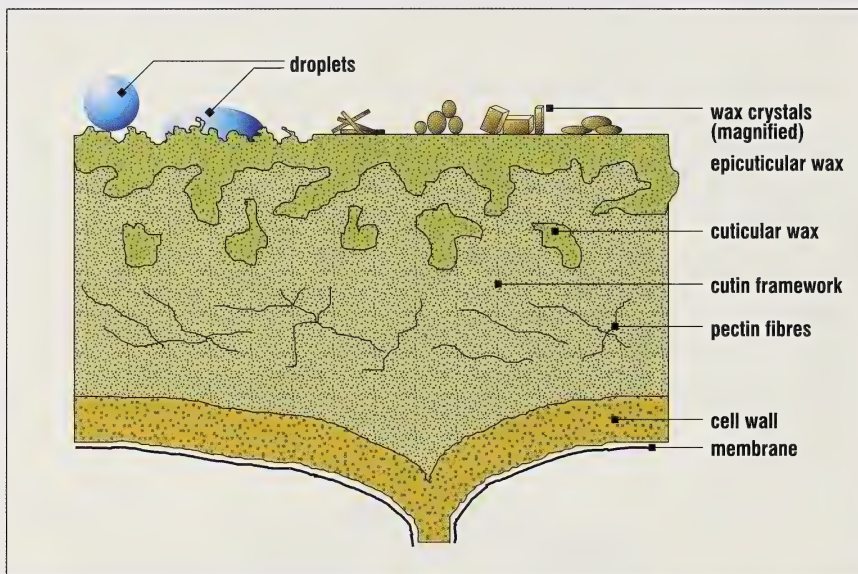
Figure 72. Cross-section of a leaf cuticle showing epicuticular and cuticular waxes and cutin, which represent a barrier of herbicide entry into plant cells.

Greater wax buildup has been related to reduced herbicide uptake, although some studies have suggested that the type of wax may be just as important as the amount. Wax type and amount differ greatly among plant species, among parts of the plant and with plant age, so no single surfactant will offer optimum benefits under all conditions.

The leaf cuticle responds to relative humidity, becoming more permeable under high humidity conditions. Spraying under these conditions has often resulted in better product uptake, but may also affect crop safety.

Since surfactants contain oil-loving components, they can interact with cuticles, helping the active ingredient enter the underlying cells. Some surfactants dissolve plant membranes, which can enhance herbicidal activity but may also threaten crop safety. For example, if membranes are disrupted before a herbicide has had a chance to translocate, the physiological isolation of the active ingredient may cause activity to decrease. There is no way to predict how individual surfactants will interact with crops, so label directions should always be followed.

Greater penetration in the presence of surfactants has been attributed to one or more of the following factors, some of which have already been discussed in this chapter:

- greater area of contact with the leaf
- increased retention at sites favorable for penetration
- reduction in evaporative loss
- solubilizing cuticular barriers
- formation of hydrophilic pathways through cuticle
- increasing permeability of membranes
- complex formation among surfactant, cuticle and active ingredient

Water quality and ammonium sulfate fertilizer

Fertilizers are useful as adjuvants for two reasons: they can overcome some antagonism caused by low-quality water and they can enhance the uptake of some herbicides by plant cells.

Ammonium sulfate (21-0-0-24) contains two useful ions that fulfill important functions. The sulfate ions (SO_4) bind with Ca^{++}, Mg^{++}, Zn^{++}, Na^+, K^+, Al^{+++} and Fe^{+++} in hard water, preventing them from inhibiting the activity of herbicides, which are susceptible to antagonism from these ions. The ammonium ions (NH_4^+) help some herbicides cross plant cell membranes, enhancing the ion-trapping effect by which these active ingredients are absorbed and translocated by cells.

Urea ammonium nitrate (28-0-0) is a liquid fertilizer that has some beneficial properties. Overall, 28-0-0 has less ammonium than ammonium sulfate (7 per cent versus 21 per cent) and contains no sulfate. The same benefits will not usually result from both, although similar results can be obtained in some instances.

Research conducted at the University of Saskatchewan has shown that hard water can reduce the effectiveness of glyphosate and 2,4-D amine. To overcome these problems, applicators should use the maximum recommended herbicide rate, or add 3 kg/100 L ammonium sulfate to glyphosate-containing sprays. The reduction of water volumes is also helpful.

Fertilizers are not effective for 2,4-D amine. In order of priority, consider (a) using an alternate source of water, (b) using the ester formulation, (c) using the maximum recommended rate and (d) using a non-ionic surfactant at 0.1 per cent v/v.

The presence of high levels of bicarbonate (HCO_3^-) in some water can antagonize the "dim" herbicides (e.g. Poast, Select, Achieve). Using the maximum recommended herbicide rate, or 1.6 L/acre liquid ammonium sulfate (0.8 kg/acre 21-0-0-24 dry), or 0.2 L/acre 28-0-0, can overcome these problems. For 2,4-D, which is also antagonized, nitrogen fertilizers do not help. Instead, use similar strategies as for hard water, or substitute MCPA if possible.

Environment

Growing conditions before and during spraying go a long way toward determining the results of adjuvant additions. Generally, when recommended herbicide rates are used under good growing conditions, the addition of extra adjuvants will not result in better weed control. When there are problems with water quality or environmental stress, however, adjuvants can play an important role.

Summary

Adjuvants lower surface tension, which can reduce droplet bounce and enhance droplet spread. In addition, they can increase herbicide absorption through cuticles and enhance the herbicide's ability to withstand adverse environmental conditions such as rain or bright sunshine. Because of the specific way in which adjuvants affect spray atomization, deposition and uptake, it is not possible to predict how any one adjuvant will interact with the many factors that govern weed control without extensive experimentation. As a result, it is important to stick to label recommendations to ensure reliable product performance.

Adjuvants are useful tools to ensure or enhance the activity of herbicides, and as a result, they are frequently included in product formulations or recommended on product labels.

Spray Drift

- wind speed and atmospheric stability are key weather factors influencing spray drift
- although higher winds increase drift, dead-calm conditions can result in even more serious drift damage
- under all conditions, coarser sprays reduce drift and are created by reducing pressure, increasing carrier volume and using specific adjuvants and low-drift nozzles
- shrouds and air assist sprays can also reduce drift by protecting droplets from wind
- reducing spray drift increases efficacy and reduces off-target damage

Factors Influencing Spray Drift

This chapter describes the factors that influence spray drift. It integrates information from all previous chapters to provide a basis for causes and solutions to this important aspect of spraying.

Although certain nozzles and shrouds can greatly reduce drift, the proper use of conventional technology is also very effective. An understanding of how weather and sprayer settings interact will help in reducing drift overall.

Weather conditions

The most important weather factors that affect spray drift are wind speed and atmospheric stability (inversions). Temperature and relative humidity may also play a role.

Wind speed – If all other factors remain constant, then spray drift will increase linearly with increasing wind speed. For example, an 8001 tip applying 50 L/ha will lose about 3 per cent drift at a 10 km/h wind speed, 7 per cent at 20 km/h and 11 per cent at 30 km/h. However, when the air is still or winds are very low, the drift cloud can move unpredictably and cause damage. Therefore, spraying is best done when there is some wind, and the operator is certain that the wind direction has stabilized.

Atmospheric stability – Temperature inversions can be the cause of considerable spray drift once a spray cloud is airborne. On a normal sunny day, the atmosphere is said to be "unstable." This term means that air near the ground is much warmer than air above. Under these conditions, there is considerable turbulence in the atmosphere, and adjacent air layers mix readily with each other. So if the air contains some drift, this drift is quickly dispersed upward and downwind, diluting it with clean air and reducing its effect (Figure 73).

Spray drift is one of the most important issues surrounding pesticide application. Sprays must reach their intended target and not be lost in the air, where they can harm people and neighbouring crops or pollute the environment.

unstable — spray cloud disperses upward and downwind

stable — spray cloud hangs over treated area in high concentration

Figure 73. Fate of a spray cloud under unstable and stable (inversion) conditions.   **Source 8**

The opposite of an unstable atmosphere is a "stable" atmosphere. This condition occurs at night, when the earth cools off, and the air near the ground is now cooler than the air above it: a situation known as a temperature inversion. Spraying under inversion conditions can lead to the long-distance transport of a drift cloud and can result in severe drift damage.

Under inversion conditions, turbulence is suppressed because adjacent air layers now do not mix with each other. In fact, the layers of the atmosphere tend to remain exactly where they are. Any drift in the air remains concentrated and may hang over the treated area for a long time. If wind speed increases, a concentrated spray drift cloud is moved away from the treated area and can cause considerable damage. The irony is that inversions are usually associated with dead-calm conditions, a time when applicators might be tempted to spray to avoid drift. The difference between stable and unstable conditions is summarized in the table below.

Impact of atmospheric stability on wind and spray behavior

Unstable conditions	Stable conditions (inversions)
sunny days	nights
some wind	calm winds
disperse spray	keep spray concentrated
predictable wind direction	unpredictable wind direction

An applicator may spray in the late evening or early morning before sunrise to avoid wind and will inevitably spray under inversion conditions. The danger with spraying under these conditions is often that the initial wind after an inversion, which is very slow and unpredictable in direction, can cause concentrated drift (which has been hanging over the field like a cloud of fog) to move to a sensitive area and cause crop damage. Most drift complaints involve spraying under inversion conditions. How long

114

do inversions persist after sunrise? After sunrise and a two to three degree rise in temperature, the inversion will most likely have burned off.

Air temperature and relative humidity – Many spray droplets evaporate to dryness between the time they leave the nozzle and when they reach the target. When the spray solution is atomized by a nozzle, spray droplets begin to evaporate. Temperature and relative humidity greatly affect how quickly these droplets evaporate. For example, under warm and humid conditions (20° C and 80 % relative humidity), a 100 μm droplet evaporates completely in 57 seconds. Under hotter, dry conditions (30° C and 50 % relative humidity), the same droplet evaporates in 16 seconds (see table on page 93).

A 50 μm droplet would last only 4 seconds under hot and dry conditions, enough time to fall only 15 cm. Droplets large enough to withstand drift may evaporate down to a size that makes them drift-prone before they can reach the target plant.

Sprayer Settings

Current drift-reducing methods focus on two approaches:

*   create coarser sprays
*   protect spray from wind

Coarser sprays

A reduction in drift-prone droplets is generally achieved by increasing the coarseness of the spray. Reduced pressure, increased carrier volume, low-drift nozzles or a drift-reducing adjuvant all create less drift-prone sprays (Figure 74).
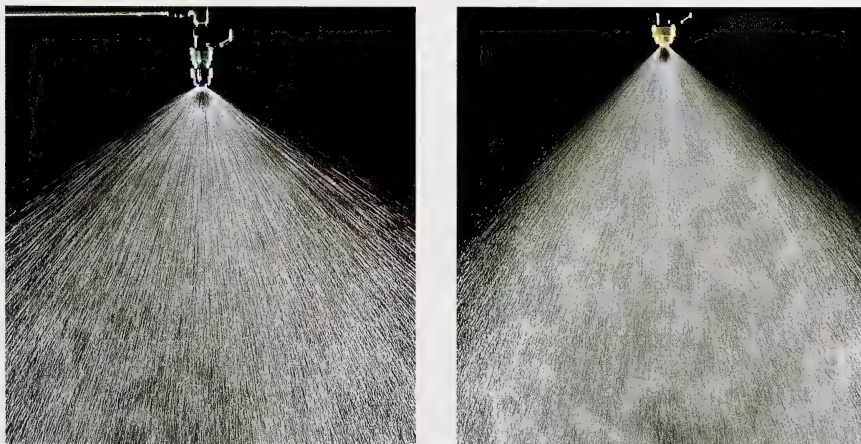
Figure 74. Coarse sprays reduce drift over sprays from standard nozzles.

Spray drift is related to the proportion of a spray contained in "drift-prone" droplet sizes. These droplets are typically less than 150 μm in diameter. But it is not quite that simple. What makes a small droplet more drift-prone is its combination of low weight and low velocity, resulting in less momentum. If a small droplet were accelerated, it would be harder for the wind to move it. That is why air assist is sometimes used to reduce drift. But in most cases, the easiest way is to reduce drift is to increase droplet size. With this strategy, the proportion of the total spray volume contained in droplets less than 150 μm is a useful indicator of drift potential.

Pressure

Droplet size is directly related to spray pressure. Higher pressures result in finer sprays, which are at greater risk of drifting. By lowering the pressure of an XR (extended range) nozzle from 40 to 20 psi, drift can be reduced significantly. XR nozzles maintain good patterns between 15 and 60 psi. However, sprayer travel speed will need to be adjusted to compensate for the lower volume output caused by reducing the pressure.

Carrier volume

Using higher carrier volumes will effectively reduce drift. If the travel speed remains unchanged, then a larger nozzle is used to apply the higher volumes. This method results in a coarser, less drift-prone spray. A second reason for less drift is that the spray solution is more diluted at the higher volume. This dilution means that drift will contain less active ingredient and will therefore have less potential for causing damage.

Low-drift nozzles

If an applicator wants the benefit of a coarser spray without changing carrier volumes, a good solution is to use low-drift nozzles. There are two basic types of low-drift nozzles – both emit coarser sprays at regular pressures and will deliver a less drift-prone spray (Figure 75 and Figures 76 and 77).
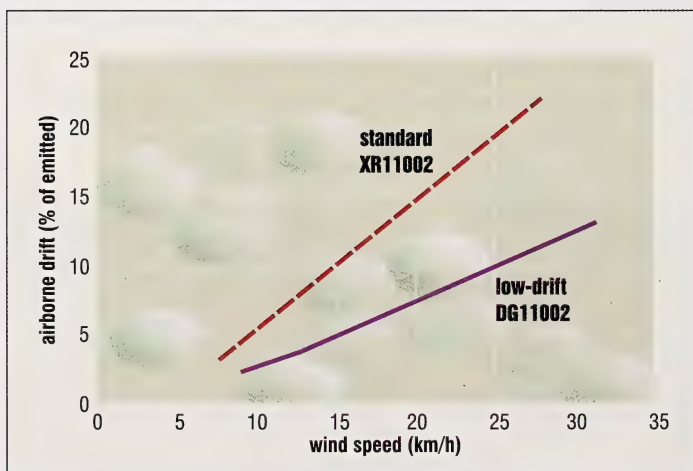

Figure 75. Effect of droplet size on off-target spray drift. Spray was applied with a self-propelled, high clearance sprayer traveling at 32 km/h and applying 30 L/ha spray solution. **Source 9**

Figure 76. Standard nozzles allow spray drift and resulting drift damage.

Figure 77. Low-drift nozzles minimize spray drift, so no drift damage results.

The first type of low-drift nozzle uses a pre-orifice design (for example Spraying Systems Drift Guard (DG) series or Lurmark's lo-drift (SD) series). These nozzles have two orifices: a "pre-orifice" meters the spray at a standard flow rate, and an "exit" orifice forms the pattern. The exit orifice is slightly larger than the pre-orifice, causing a lower-pressure spray to be emitted. This change in pressure is transparent to the user, allowing the pressure gauge to read 40 psi even though the exit tip is only operating at 20 psi.

As a rule, using a low-drift nozzle provides the same droplet size spectrum as the next larger conventional nozzle. In other words, a DG8002 has a similar size spectrum as an XR8003, and a DG 8003 has the size spectrum of an XR8004 and so forth. In research trials, spray drift from an XR11002 was cut in half by using a DG11002 tip. Lurmark nozzles were equally effective.

The Turbo TeeJet (TT) series use a different approach to creating a coarser spray. A turbulence chamber built into the nozzle mixes the spray solution before it forms a pattern, creating larger droplets. This approach has the advantage of allowing for a much wider pressure operating range. While DG nozzles can be operated between 30 and 60 psi, TT nozzles maintain good patterns between 15 and 90 psi. For automatic flow rate regulators, which use pressure to adjust flow rate in response to changing travel speeds, wider operating ranges can be an advantage.

The second type of low-drift nozzle, referred to as "venturi" or "air-inclusion" nozzles, are even more effective at reducing drift. A venturi design draws air into the nozzle, which then mixes with the spray. A very coarse, air-laden spray is emitted through the exit tip. Droplets contain air bubbles, which enhances retention of the coarser spray. The drift reduction from these venturi nozzles is significantly better than from previous low-drift technologies. Efficacy data suggest that these nozzles perform well with most herbicides, notably Group 2, 4, 9 and 22. For Group 1, 6 or 10 herbicides and with difficult-to-wet weeds, such as lamb's-quarters, wild oats or foxtail, caution is advised.

Drift-reducing spray adjuvants

Adjuvants – usually starch, polyvinyl or polyacrylamide polymers – are also effective at increasing the spray coarseness. These are not very prevalent in Canada, but might appear under the trade names "Nalcotrol," "38-F" or "Lo-Drift." These products work by increasing the viscosity of the spray solution, which reduces the number of fine droplets. Unfortunately, these polymers may have some drawbacks that applicators need to understand:

- the effect drift-reducing adjuvants have on herbicide efficacy in the field is not known. As with the low-drift tips, efficacy may be affected for some products.
- these adjuvants change the spray pattern emitted by a conventional nozzle. A flat fan spray will become narrower, resulting in the reduced overlap of adjacent fan patterns and increasing the likelihood of misses. Boom height may need to be increased to compensate for this effect, which offsets the desired drift reduction.
- in addition to the narrowing of the spray angles, patterns become more erratic, with more spray volume at the overlap of the nozzles and less underneath it (Figure 78). This situation can result in uneven weed control across the width of the boom.
- some drift reducing adjuvants degrade rapidly under pump shear stress. If the spray solution is agitated through the pump more than two to three times, the adjuvant degrades and loses most of its effectiveness. Choose shear-resistant adjuvants.

In the future, new low-drift adjuvant technologies will address the above concerns. Some of these technologies are already available in the US, but are not yet approved for use in Canada.
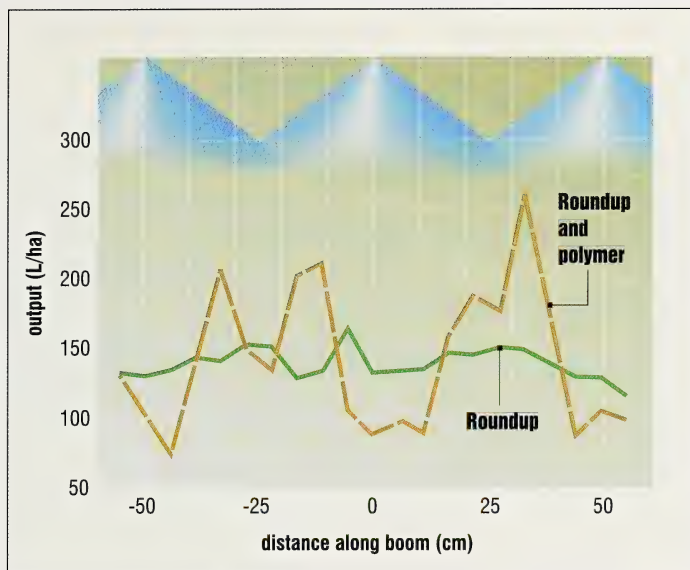
Figure 78. Effect of a drift-reducing adjuvant on the spray pattern of Roundup. Nozzle was an XR8003 at 40 psi pressure, traveling at 8 km/h.   **Source 10**

Protecting sprays from wind

Drift-prone droplets can be protected from the wind by reducing sprayer travel speed, lowering the boom, using shrouds or using a properly adjusted air assist.

Travel speed – Historically, sprayers have operated at slow travel speeds (8 to 10 km/h) and were able to maintain a constant height along the width of the boom. Recently, the use of self-propelled high clearance sprayers has increased. These sprayers use a floating, self-supporting boom and can travel at speeds up to 35 km/h.

Faster travel speeds have two main effects on how spray behaves after it leaves the nozzle. First, faster travel speeds cause increased air shear stress on the spray sheet emerging from a nozzle. This effect increases sheet breakup and causes a finer, more drift-prone spray to be produced. Secondly, the faster speed causes the spray to stay aloft longer because it gets swept back due to air resistance. The net result is a finer spray more exposed to winds that can move the spray off-target. Research tests have confirmed that faster travel speeds increase drift, even when applicators use a coarser spray (Figure 79).
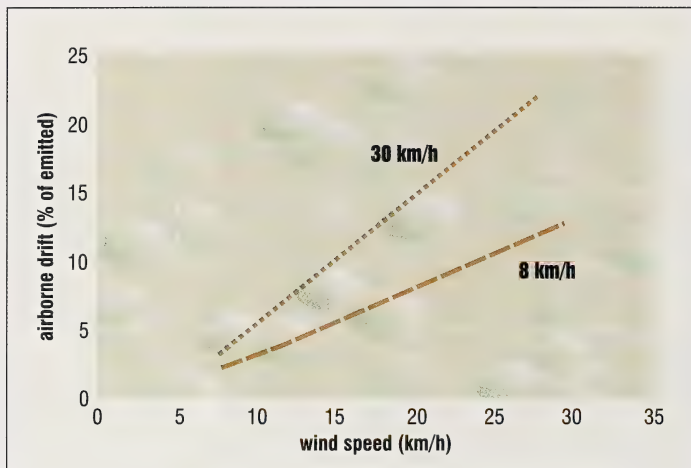
Figure 79. Effect of travel speed on spray drift: 30 km/h travel speed conducted using XR11002 tips applying 30 L/ha and 8 km/h travel speed done using XR8001 tips applying 50 L/ha.
Source 11

Boom height – Spray can be protected from the wind by lowering the boom to the minimum recommended setting. For 80° fan angles, this setting is 45 cm and for 110° fan angles, 35 cm. The ability to lower 110° nozzles closer to the ground does not really afford more drift protection because 110° nozzles create finer sprays than 80° nozzles. In addition, suspended booms of self-propelled sprayers are likely to sway during operation, so booms need to be high enough to compensate. By orienting the spray forward, boom height can be reduced as long as the proper nozzle-to-target distance is maintained.

Shrouds – Shrouds reduce drift. In field testing, shrouds reduced drift from an 8001 tip applying 50 L/ha approximately 70 per cent (Figure 80). Drift from the finer spray produced by an 11001 tip was slightly greater. Unfortunately, no data is available on the performance of shrouds on high clearance sprayers moving at faster travel speeds. Shrouds should be expected to be less effective at the higher travel speeds.
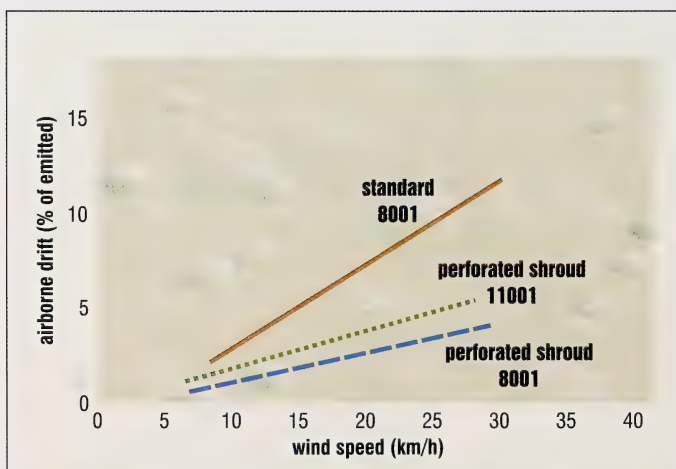
Figure 80. Reduction of drift with shrouds. Application volume was 50 L/ha.
Source 12

Some booms cannot accommodate shrouds. In those situations, cones may be appropriate. Cones allow greater ground clearance for suspended booms and will not contaminate susceptible crops with spray residue on the shielding material. Protective cones have been shown to reduce drift by 30 to 50 per cent (Figure 81).

Figure 81. Shrouds and cones can reduce spray drit.

Air assist – Using air assist to reduce drift is sound in principle, but more difficult to put into practice. In principle, a fast-moving droplet is more drift-resistant than a slow-moving droplet of equal size. Air assist involves the use an air stream to carry the emitted spray downward to the target, imparting speed and preventing it from hanging in the air and being exposed to wind (Figure 82).
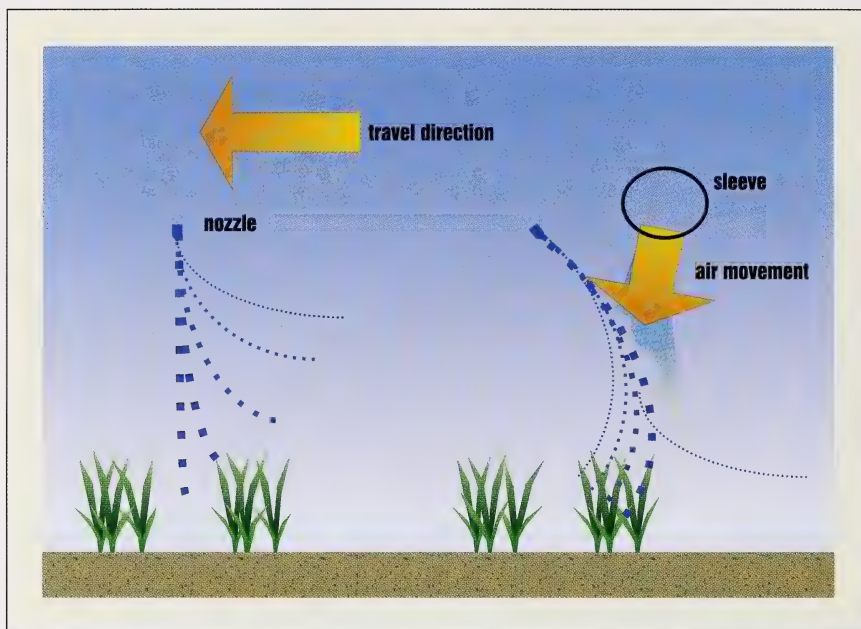
Figure 82. Air assist carries drift-prone droplets to their intended target.

It is important to set the direction and velocity of the air blast to match travel speed, wind and crop canopy conditions. For example, too strong an air blast into a small crop canopy such as seedling wheat can result in the air blast rebounding off the ground. Any spray not intercepted by the canopy will return upward into the airstream and be prone to drifting. Tests have shown that drift increases if the air blast is too strong. When spraying into a dense canopy, for example to desiccate a pulse or apply fungicide to canola, a strong air blast is more appropriate to obtain better canopy penetration. Ultimately, the air assist must be adjustable to be useful, and it takes an experienced operator to obtain the maximum benefits.

Droplet Size and Efficacy

Always consider the possible effect of a change in droplet size on product efficacy by studying the nature of the weed to be controlled. While drift can be minimized by using a coarser spray, these coarser sprays may not always be retained as well by difficult-to-wet weeds (grasses such as foxtail and broad-leaves such as kochia). Easy-to-wet plants, such as pigweed or smartweed, actually prefer coarser sprays.

When applying the recommended rate of herbicides, these effects should not pose a problem with low-drift nozzles. But reducing the rate may result in less consistent weed control. Although the new "venturi" type low-drift nozzles work well despite their

large droplets, the use of common sense is still important when predicting whether a coarse spray is appropriate for a weed or herbicide. A low-drift nozzle will work well under most conditions.

When conditions become challenging, such as under later staging, poor growing conditions, lower rates or lower pressures, emphasis should be placed on higher carrier volumes with low-drift nozzles.

Importance of Active Ingredient

Applicators need to be aware of the potency and vapor pressure of the herbicide's active ingredient because some herbicides are prone to vapor drift. The application of volatile products should be avoided either on or just before hot days because vapor drift increases with higher air temperatures.

The actual amount of spray leaving a treated area and settling out downwind is very small – some studies report that only one per cent or less of the applied amount is deposited a significant distance downwind under unstable (daytime) conditions. The damage caused depends on the potency of the active ingredient and the plant's susceptibility to the herbicide.

For example, Group 2 and 4 herbicides are very active and can damage susceptible crops at minute doses. Although these products do not drift more than others, the fact that they damage crops at small doses means applicators must take extra care. Most other products are less active, and small quantities have little noticeable effect on crops. However, little is known about how native plants and animals respond to low pesticide doses over many years, so precautions must be taken to ensure sprays land only where they should.

The following table provides a summary of drift-reducing strategies.

Some herbicides are prone to vapor drift. Vapor drift can occur even when there is no particle (droplet) drift, and even dry spray deposits can send vapors into the atmosphere.

Pros and cons of various drift-reducing strategies

Drift reducing strategy	Pro	Con
Wait for ideal weather conditions	Best strategy	May have to wait too long
Reduce travel speed	More entrainment of the spray cloud, protects fines	Slower work rates
	Other drift reducing strategies (shrouds, air-assist, low-drift tips, etc.) become more effective	At constant carrier volume, smaller nozzle needed, which produces finer spray
Use low-drift tips	Fewer drops prone to drifting	Possible changes in spray retention and efficacy
	No change in work rate	Need extra set of tips
Increase carrier volume	At same travel speed, requires larger nozzle, which produces less drift-prone spray	Reduced efficiency due to more frequent re-fills
	Spray solution more diluted, creating less potent drift	Reduced effectiveness of glyphosate sprays
Install protective shield	Protects spray from wind	Reduced visibility of spray nozzles and patterns
	Permits use of conventional spray nozzle and volumes	Shroud decontamination needed between crops or herbicides
Lower boom height	Spray less exposed to wind	May be difficult to maintain proper clearance on self-supporting boom
Reduce pressure	Creates coarser spray	Must reduce travel speed to maintain constant carrier volume
	No need for extra set of tips	Pattern may change reduced pressure range available for automatic flow controllers
Low-drift adjuvant	Creates coarser spray	Creates non-uniform spray pattern
	No need to change nozzles or pressure	May degrade under pump shear stress
	May reduce droplet rebound	May need to raise boom to correct pattern

Weed Science and Herbicide Information Sources

Weed science is multi-disciplinary; therefore, information about herbicides, weeds and herbicide application appears in a wide range of publications.

Journals

Agronomy Journal

Annals of Applied Biology

Canadian Journal of Botany

Canadian Journal of Plant Science

Crop Protection

Pesticide Biochemistry and Physiology

Pesticide Science

Planta

Plant Physiology

Weed Research

Weed Science

Weed Technology

Books on herbicides and their application

Application Technology for Crop Protection (1993) G.A. Matthews and E. C. Hislop (eds.), Wallingford, UK; CAB International.

Atomization and Sprays (1989) A.H. Lefebvre, New York; Hemisphere Publishing Corporation.

Biochemistry and Physiology of Herbicide Action, (1982) C. Fedtke, Berlin, New York; Springer-Verlag.

Field Sprayers for Pesticides, R. Grover and W. B. Reed (eds.), Agriculture Canada Publication 1849/E.

Herbicide Activity: Toxicology, Biochemistry and Molecular Biology, (1997) R. Michael Roe, James D. Burton, Ronald J. Kuhr, Amsterdam, Washington, Tokyo; IOS Press.

Herbicides: Chemistry, Degradation and Mode-of-Action, (1987) P. Kearney and D. Kaufman, 2nd edition 1975 NY; M. Dekker.

Methods of Applying Herbicides, vol. 4. (1987) C.G. McWhorter and M. R Gebhardt (eds.), Monograph Series of the Weed Science Society of America, Champaign, IL; Weed Science Society of America.

Microclimate and Spray Dispersion, 1st ed., (1992) D.H. Bache and D. R. Johnstone, London; Ellis Horwood Ltd.

Pesticide Application Methods (1979) G.A. Matthews, London; Longman Group.

Physiology of Herbicide Action, (1993) M. D. Devine, S. O. Duke and C. Fedtke, Englewood Cliffs, NJ;PTR Prentice Hall.

Target Sites for Herbicide Action, (1991) R. C. Kirkwood (ed.), New York, Plenum Press.

TeeJet Agricultural Spray Products Catalog, #45A, (1996) Anonymous, Spraying Systems Co., P.O. Box 7900, Wheaton, IL 60189-7900. Distributed in Canada by John Brooks Co. Ltd., 2625 Meadowpine Blvd., Mississauga, ON L5N 7K5

The Herbicide Glyphosate, (1985) E. Frossbard and D. Atkinson, London, Boston; Butterworths.

The Imidazolinone Herbicides, (1991) D. Shaner and S. L. O'Conner, CRC Press; Boca Raton.

The leaf surface of major weeds, (1991) J. Harr, R. Guggenheim, G. Schulke and R.H. Falk, Witterswill, Switzerland; Sandoz Agro Limited.

Weed Physiology Vol. II., (1985) S.O. Duke, Boca Raton, FL; CRC Press.

Other references

Herbicide Handbook of the Weed Science Society of America

WSSA, 1508 West University Ave., Champaign, IL,USA 61821-3133

Web sites

Weed Science Society of America
   http://ext.agri.uiuc.edu/wssa/

International Survey of Herbicide Resistant Weeds
   http://weedscience.com

Alberta Agriculture, Food and Rural Development
   http://www.agric.gov.ab.ca

Saskatchewan Agriculture and Food
   http://www.agr.gov.sk

Manitoba Agriculture
   http://www.gov.mb.ca

Agriculture and Agri Food Canada
   http://www.agr.ca

University of Saskatchewan Extension
   http://www.extension.usask.ca/

Source List

Source 1   Young, B. W. 1986. The need for a greater understanding in the application of pesticides. Outlook on Agriculture 15:80-87.

Source 2   Doble, S. J., G. A. Matthews, I. Rutherford and E. S. E. Southcombe. 1985. A system for classifying hydraulic nozzles and other atomisers into categories of spray quality. Proc. 1985 Brit. Crop Prot. Conf. – Weeds 5:1125-1133.

Source 3   Anonymous, 1996. TeeJet Agricultural Spray Products Catalog, #45A, Spraying Systems Co., P.O. Box 7900, Wheaton, IL 60189-7900. Distributed in Canada by John Brooks Co. Ltd., 2625 Meadowpine Blvd., Mississauga, ON L5N 7K5

Source 4   Matthews, G. A. 1979. Pesticide Application Methods. Longman Group, London, 336 pp.

Source 5   Matthews, G. A. 1979. Pesticide Application Methods. Longman Group, London, 336 pp.

Source 6   Matthews, G. A. 1979. Pesticide Application Methods. Longman Group, London, 336 pp.

Source 7   Berndt, G.F. 1987: Efficiency of foliar sprays as influenced by the inclusion of surfactants. Res. Devel. Agric. 4:129-139.

Source 8   Bache, D. H., T. J. Lawson, and S. Uk. 1988. Development of a criterion for defining spray drift. Atmospheric Environ. 22:131-135.

Source 9   Grover, R., Caldwell, B.C., Maybank, J and Wolf, T.M. 1997. Airborne off-target losses and ground deposition characteristics from a Spra-Coupe using "low drift" nozzle tips. Can. J. Plant Sci. 77:493-500.

Source 10   Downer, R. A., T. M. Wolf, A. C. Chapple, F. R. Hall and J. L. Hazen. 1995. Characterizing the impact of drift management adjuvants on the dose transfer process. Pages 138-143 *In:* R. E. Gaskin (ed.) Fourth International Symposium on Adjuvants for Agrochemicals. New Zealand Forest Research Institute, Rotorua, NZ.

Source 11   Grover, R., Caldwell, B.C., Maybank, J and Wolf, T.M. 1997. Airborne off-target losses and ground deposition characteristics from a Spra-Coupe using "low drift" nozzle tips. Can. J. Plant Sci. 77:493-500. and Wolf, T. M., R. Grover, K. Wallace, S. R. Shewchuk, and J. Maybank. 1993. Effect of protective shields on drift and deposition characteristics of field sprayers. Can. J. Plant Sci. 73:1261-1273.

Source 12   Wolf, T. M., R. Grover, K. Wallace, S. R. Shewchuk, and J. Maybank. 1993. Effect of protective shields on drift and deposition characteristics of field sprayers. Can. J. Plant Sci. 73:1261-1273.

Glossary

Adjuvant – Any substance in a pesticide formulation or added to the spray tank to modify biological activity or application characteristics. There are two classes of adjuvants: activators form one class, spray modifiers and utility modifiers the other.

Air Assist – The use of an air blast to help transport spray to its target. Some air systems use hydraulic nozzles to atomize the spray and merely transport it to the target. Others systems use air to atomize the spray (air-shear nozzles). The latter systems tend to produce finer sprays and use stronger air blasts.

Anemometer – A device for measuring wind speed. Vane-anemometers are available in compact models and are more portable than cup anemometers.

Apoplast – The part of the plant outside the cell membrane, including the cell wall. It is usually considered non-living, a space filled with water and dissolved substances. The apoplast is contiguous with the xylem.

Atomization – The energy-consuming process of converting a liquid from a continuous fluid into a cloud of smaller particles. Energy can be in the form of hydraulic pressure (e.g. flat fan nozzles), air shear (e.g., some air assist booms), centrifugal force (e.g., spinning disks) and electrostatic energy (some electrostatic nozzles).

Auxin – Plant growth regulator that plays a key role in cell extension, division and differentiation during the course of the plant life cycle. Auxins influence other growth regulators, including ethylene, abscisic acid and cytokinins.

Capture efficiency – A measure of the ability of a target to intercept incoming droplets. Small droplets are captured most efficiently by small objects, whereas large droplets are captured most efficiently by larger objects. An increase in droplet velocity usually increases capture efficiency, assuming no droplet rebound.

Carrier volume – The amount of carrier (usually water) in which the crop protection agent (CPA) is applied per unit area. Typical volumes for most ground-applied CPAs range from 50 to 200 L/ha, but may be much greater in orchard applications

Cell membrane – A double layer of phospholipids, with embedded proteins, that surrounds all living cells, plant and animal. The cell membrane regulates movement into and out of the cell and separates the living from the non-living parts of the cell.

Chlorosis – Loss of green color in foliage followed by yellowing or whitening of the tissue.

Coefficient of Variation (CV) – A measure of variability. By definition, the CV is the standard deviation of a data set expressed as a percentage of the mean, i.e., CV = standard deviation / mean * 100.

Contact angle – The angle between the leaf surface and the leading edge of the droplet.

Contact herbicide – A herbicide that is phytotoxic by contact with plant tissues rather than as a result of translocation.

Crop Oil Concentrates (COCs) – Vegetable or petroleum oils mixed with emulsifiers whose primary function is to enhance the uptake of a herbicide into the plant.

Cuticle – The often waxy outer layer of plant epidermal cells. The cuticle is comprised of a cutin framework that extends from the cell wall. Waxes are embedded in, and form the outer surface of, this framework. Cuticles are designed to reduce water loss from the plant and also to form a barrier of entry to CPAs. The cuticle has the ability to absorb water, and can become hydrated under humid conditions. In this state, it is often more permeable to water-soluble substances.

Desiccant – Any substance used to accelerate the drying of plant tissue.

Dose transfer – The cumulative steps and processes involved in getting the active ingredient from the source (usually the nozzle) to the target. The target of the active ingredient in dose transfer is somewhat arbitrary and may depend on the pest. For a weed, the target could be the leaf surface or its cellular site of action.

Drift – The movement of a CPA from its intended target area in an air flow (wind). There are two types of drift: particle drift refers to the movement of liquid droplets or dry active ingredient while vapor drift refers to the movement of active ingredient in a vapor form. Vapors can emanate from a liquid or dry deposits. Particle drift is primarily a function of particle size and wind velocity, whereas vapor drift is governed by the vapor pressure (volatility) of an active ingredient, the ambient temperature, and wind speed (remember that vapor pressure increases with temperature and that the vapor pressures of various gases are independent of each other. In other words, high relative humidity will reduce the evaporation of water, but not of 2,4-D).

Droplet size spectrum – The range of droplet sizes in a spray. A droplet size spectrum is usually described using several parameters, most commonly the number median diameter (NMD) and volume median diameter (VMD). Recently, sprays have been classified according to a system developed in the UK, where several size spectrum parameters were used to define spray quality as fine, medium, coarse, etc.

Droplet size – Diameter of a spherical droplet, usually expressed in micrometres (μm). There are 1000 μm in a millimetre.

Electrostatics – The use of electrical energy to charge a spray solution or spray cloud, resulting in droplets of like charge being emitted by an atomizer. These droplets are attracted to grounded objects, although the attraction is weak and does not come into play until the droplets and targets are very close to each other.

Emulsifier – A surfactant made up of both hydrophilic and hydrophobic portions. When an emulsifier, an oily herbicide and water are mixed, the emulsifier forms spheres with oily herbicide droplets on the inside. It facilitates the suspension of oil-like herbicides in water.

Enzyme – A protein that regulates and promotes the synthesis and degradation of organic compounds. Enzymes are composed of amino acids in chains, folded into functional shapes.

Epinasty – More rapid growth on the upper surface of the plant part (especially leaves), causing it to bend downwards.

Ethylene – A naturally occurring plant growth regulator, in the form of a gas.

Growth regulator – A substance used for controlling or modifying plant growth processes without significant phytotoxic effects at the dosage applied.

Hydraulic nozzle – A nozzle that uses hydraulic pressure to achieve atomization. In its most basic form, a hydraulic nozzle is comprised of an orifice that creates a liquid sheet, which eventually becomes unstable and breaks up into droplets, when pressurized liquid is forced through it.

Hydrophilic / Lipophobic – Water-loving or oil-hating. These terms are used to describe how substances will behave in a water or oil environment. Hydrophilic substances have some solubility in a polar or aqueous system.

LD$_{50:}$ – Lethal dose of 50% – the dose that would be predicted to kill 50% of the test subjects. A range of animals are used for testing herbicides, including fish and mammals. Throughout this document, the LD$_{50}$ for rats has been used for ease of comparison.

Lipophilic / Hydrophobic – Oil-loving or water-hating. These terms are the opposite of hydrophilic / lipophobic. Lipophilic substances have some solubility in a non-polar or oil system.

Low-drift nozzle – A modified hydraulic nozzle that creates a coarser spray at the same flow rate as a standard nozzle. Drift reduction is achieved by reducing the proportion of the total spray volume which is emitted in drift-prone droplets (i.e., those less than 100 μm in diameter) via a pressure drop, turbulence or air induction.

Metabolism – Changing a herbicide molecule from one form to another, usually by breaking up the herbicide molecule or by adding onto it. Metabolism can be enzyme mediated.

Monodisperse spray – Spray containing droplets of uniform size.

Necrosis – Localized death of living tissues.

Non-selective herbicide – A chemical that is phytotoxic to plants without regard to species. Plant death may be a function of dose, method of application or timing.

Patternation – Measurement of the uniformity of spray output along the width of the boom. Under static (stationary) conditions, a plastic patternator that collects spray in channels is used. For dynamic patternation, the sprayer is moved over a collector at field speed. Collectors may be water-sensitive cards, string, petri-plates, plastic strips, etc. A tracer dye is usually added to the spray tank to permit quantification of the small amount of dye required for this technique. Dynamic CVs tend to be greater than static CVs.

Persistent herbicide – A herbicide that when applied at the recommended dose, will harm susceptible crops planted in a rotation in subsequent years.

Phloem – Transport system in plants that moves sugars and amino acids both up and down. Sugars move through phloem cells, which are living. The general direction of phloem transport can change during the day and throughout the growing season. To reach the roots, a foliar-applied herbicide must be translocated in the phloem.

Polydisperse spray – Spray containing droplets of different sizes

Proherbicide – Biologically inactive chemical form of the herbicide. Some herbicides are applied in this form. Plants have the capacity to change the proherbicide into a toxic molecule. Herbicides are formulated as proherbicides because they are better than the active molecule in penetrating the cuticle, are more stable in formulation or are less volatile.

Psychrometer – An instrument for determining the relative humidity of air. Two conventional thermometers are exposed to the atmosphere: one has a wet sleeve surrounding its bulb, the other is unmodified. The unmodified thermometer measures the air temperature (dry bulb temperature); the other measures the wet bulb temperature. The wet bulb temperature will be lower than the dry bulb temperature because water evaporates from the sleeve, cooling the bulb. This rate of evaporation depends on the relative humidity of the air. Charts are used to convert temperatures to relative humidity.

Selective herbicide – A herbicide that affects some plants but not others. Most herbicides are selective; for example, Group 1 herbicides do not affect broad-leaved weeds or crops and are thus selective. Glyphosate or Roundup is not selective.

Spray retention – The ability of a spray to hit and remain in contact with a target surface.

Stop distance – The distance a particle at a known speed travels prior to reaching terminal velocity.

Surface tension – A property of a liquid that resists the expansion of the liquid surface area. Surface tension forces must be overcome by aerodynamic, pressure, centrifugal or electrostatic forces to achieve atomization. They must also be overcome to achieve droplet spread on a leaf surface.

Surfactant – An adjuvant that has surface active properties. It improves the emulsifying, dispersing, spreading, wetting, or other properties of a liquid by modifying its surface characteristics. Surfactants can lower surface tension of a liquid, which may enhance droplet spread, reduce droplet rebound, and enhance active ingredient uptake.

Symplast – The inside, living part of a cell, enclosed by the cell membrane.

Synergism – Complementary action of different chemicals such that the total effect is greater than the sum of individual effects.

Systemic herbicide – Herbicide that translocates in the phloem or xylem. Most herbicides move in the plant to some extent.

Terminal velocity – The velocity of an object falling through air without the assistance of external energy. When a droplet is emitted from a nozzle, it has been accelerated by the pressure at the nozzle. This initial speed is quickly reduced by air resistance. Once the counteracting forces of gravity and viscous drag have reached equilibrium, the droplet travels at its final, or terminal, velocity.

Tolerance – The capacity to withstand herbicide treatment with minimal effects.

Translocation – The movement of the active ingredient within the plant from its site of uptake to another plant region. Movement of a herbicide in the phloem or xylem. The rate of translocation differs between herbicides and can change with the age of the plant or the environmental conditions. Perennial weed control depends on the translocation of the herbicide to distant roots or rhizomes.

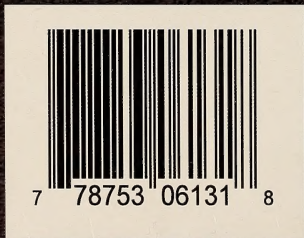**Uptake** – The absorption of the active ingredient into the underlying plant tissue.

Viscosity – A liquid property that describes the ability to resist flow.

Weed – A plant growing where it is not wanted.

Wetting agent – See surfactant.

Wettability – The properties of a surface that define how easily a liquid will adhere to and spread on it. In general terms, an easy-to-wet surface can be wetted with plain water, whereas a difficult-to-wet surface requires the addition of surfactants to achieve wetting. Wettability is related to the leaf surface microstructure, that is, the type, amount and three-dimensional appearance of cuticular wax deposits. The presence of leaf hairs (trichomes) can also affect wettability.

Xylem – One-way transport system in plants that moves water and dissolved minerals from the roots to the shoots. Water moves through dead cells that function like small pipes. Plants control water loss and thus xylem transport by opening and closing stomata, but environmental factors such as available soil moisture, temperature, humidity and wind also have a major impact on the rate of water movement in the xylem. Some herbicides move in xylem.